# Separation and conversion of nuclear spin isomers of ethylene

**5 AUTHORS**, INCLUDING:

Pavel L. Chapovsky
Russian Academy of Sciences

**94** PUBLICATIONS **933** CITATIONS

# Separation and conversion of nuclear spin isomers of ethylene

P.L. Chapovsky [*], J. Cosléou, F. Herlemont, M. Khelkhal, J. Legrand

*Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, CERLA, Centre d'Etudes et de Recherches Lasers et Applications, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France*

Received 15 February 2000; in final form 7 April 2000

## Abstract

First separation of the nuclear spin isomers of ethylene molecules ($^{13}C^{12}CH_4$) and determination of the isomer conversion rate are reported. Experiment has revealed a linear increase of the conversion rate versus gas pressure equal to $(5.2 \pm 0.8) \cdot 10^{-4}$ s$^{-1}$/Torr. This indicates that the isomer conversion in $^{13}C^{12}CH_4$ is governed by quantum relaxation. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The nuclear spin isomers of molecules (a familiar example is the *ortho* and *para* hydrogen) have fundamental importance in molecular physics. Nuclear spin states are the most stable molecular states. For example, the hydrogen isomer decay time is $\approx 1$ year at the pressure 1 atm and room temperature [1]. Isomer relaxation is due to very weak intramolecular forces, or to very small intermolecular cross-sections. Nuclear spin isomers give rise to the famous line intensity alternation effect which is well known in spectroscopy and astrophysics. Moreover, there are some practical applications of molecular spin isomers, e.g., for selective chemical reactions [2,3], or for significant enhancement of the NMR signals [4,5].

Although investigations of molecular spin isomers have been started as early as 1929 [6], there are just a few molecules for which progress has been achieved. The isomer separation has been performed so far only for $H_2$ [6], $CH_3F$ [7], $H_2O$ [8], $CH_2O$ [9], $Li_2$ [10], and $H_3^+$ [3]. Except for the hydrogen molecules, the isomer separation faces big difficulties which are caused by almost identical physical and chemical properties of the species. Development of the separation methods is also complicated by the fact that even the order of magnitude of the isomer conversion rate is not known in advance.

In the present Letter we report the first separation of nuclear spin isomers of ethylene molecules and the experimental data on their conversion rates.

## 2. Nuclear spin isomers of ethylene

In this work we study the isomers of the ethylene molecule $^{13}C^{12}CH_4$. This molecule was chosen because of convenient coincidences between the $^{13}C^{12}CH_4$ absorption lines and the $CO_2$ laser lines.

---

* Corresponding author. Permanent address: Institute of Automation and Electrometry, Russian Academy of Sciences, 630090 Novosibirsk, Russia. E-mail: chapovsky@iae.nsk.su

The $^{13}$C$^{12}$CH$_4$ molecule is a planar nearly symmetric prolate top which has the $C_{2v}$ group of symmetry [11]. Each rotational state is determined by the molecular angular momentum $J$, its projection on the molecular symmetry axis, $K_a$, and quantum number $K_c$. The quantum number $K_c$ can only take the values $J - K_a$ and $J + 1 - K_a$. In the ground electronic and vibrational state, the rotational states having even $K_a$ quantum numbers are the *ortho* species for which both symmetric pairs of protons are either in a singlet, or in a triplet spin state. The *ortho* states have nuclear statistical weight equal to 10. States having odd $K_a$ values (*para* species, nuclear statistical weight equal 6) have one pair of symmetrical protons in a singlet spin state but the other pair in a triplet spin state.

Absorption spectra of $^{13}$C$^{12}$CH$_4$ at 10 μm range is dominated by the $\nu_7$ fundamental band which is out-of-plane, $c$-type bending mode [12]. There are number of coincidences between the $^{13}$C$^{12}$CH$_4$ absorption lines and the CO$_2$-laser lines. The best set of the molecular parameters of $^{13}$C$^{12}$CH$_4$ is given in Ref. [13,14]. The absorption spectrum is not dense having well resolved *ortho* and *para* absorption lines.

## 3. Experiment

Similar to the enrichment of the spin isomers of CH$_3$F performed previously (for the review see [15]) we have used in this work the Light Induced Drift (LID) effect [16] in order to separate the spin isomers of ethylene molecules. The LID effect of ethylene molecules was previously studied in Refs. [17–19] where LID produced separation of ethylene and foreign buffer gases.

For the convenience of the reader we briefly describe the principle of the LID effect. Let us consider a monochromatic laser beam absorbed by the molecules in the presence of large amount of buffer particles. If the frequency of radiation is tuned to, e.g., red wing of the Doppler absorption profile, radiation will interact only with the molecules moving towards the laser. Note that this velocity selective excitation occurs only at low gas pressures when the homogeneous linewidth is much smaller than the

Doppler width of the absorbing transition. Because the mean free path of the absorbing molecules is changed upon excitation (due to the change of the cross-section), e.g., becomes smaller, the molecular Brownian motion occurs with anisotropic mean free paths which results in a flux of the absorbing molecules as a whole. The buffer particles flow to an opposite direction due to the momentum conservation law. Note that the momentum transfer from the radiation to the gas was neglected. In a tube with close ends, the fluxes result in a spatial separation of the two gas components.

The use of a two component gas mixture (absorbing and buffer particles) is essential for the LID effect. The two spin isomers of $^{13}$C$^{12}$CH$_4$ perfectly serve for this purpose because their absorption spectra are well resolved. In the present work we separate the spin isomers of the same molecule. This brings new important features to the experiment in comparison with the previous investigations of LID of ethylene in foreign gases [17–19] because the separated species are not stable molecules and can convert into the other. Furthermore, the absorption line used to produce the LID effect and the combination absorbing-buffer particles are both different from Refs. [17–19].

A schematic of the experimental setup is shown in Fig. 1. The separation of isomers were produced in a glass capillary (having the inner diameter 1 mm and the length 1 m) by ≈ 15 W radiation of a CO$_2$-laser (PL5, Edinburgh Instruments). The laser was tuned to the P(24) line from the 10.6 μm band of CO$_2$ and
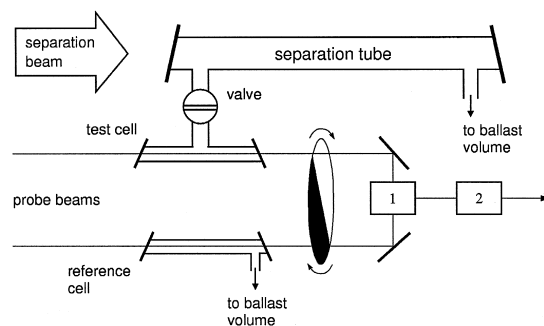


Fig. 1. Schematic of the experimental setup. (1)-detector; (2)-lock-in amplifier. The rear side of the separation tube and the reference cell are connected to the same ballast volume to ensure an equilibrium isomer composition in these places.

had its frequency stabilized to the maximum of the $CO_2$ laser gain profile. The laser radiation was absorbed in the separation tube by the transition $(14,5,10) \rightarrow \nu_7(15,4,12)$ which belongs to *para* $^{13}C^{12}CH_4$ molecules. (The numbers in brackets indicate $J$, $K_a$, and $K_c$, respectively.) Detuning of the laser frequency from the absorption line center is $\omega_{laser} - \omega_0 = -36 \pm 6$ MHz [14]. This absorption line is well resolved. The closest neighbouring absorption line (*ortho* line $(18,2,17) \rightarrow \nu_7(17,3,15)$), is by $\approx 400$ MHz away. The ethylene gas having nearly 90% purity of $^{13}C^{12}CH_4$ isotope modification was used in the experiment.

Detection was done with the help of radiation from an additional waveguide $CO_2$-laser tuned to the 10P8 line which frequency almost coincides with the center of the $^{13}C^{12}CH_4$ absorption *para* line $(7,1,6) \rightarrow \nu_7(8,0,8)$ [14]. To improve stability of the detection system, the frequency of the waveguide laser was locked to the center of the ethylene absorption line.

To measure the isomer conversion rate we have performed the following steps. First, signals from the two arms of the detection system were approximately equalized using an ethylene gas having equilibrium isomer composition in the test and reference cells. Then the strong laser beam inducing the drift was applied and the isomer separation started. After sufficient enrichment was achieved, the valve was closed and the detection system monitored the conversion process. Examples of the decay curves are given in Fig. 2. These data were fit by the function $a\exp(-\gamma t) + b$, where $\gamma$ is the conversion rate of the isomers and $b$ accounts for the signal offset. This offset was removed for the curves in Fig. 2. Using the fitting function having an offset was convenient because it compensates possible inaccuracy of the initial equilibration of the two detection arms. An offset accounts also for some spurious contributions to the signal which appear, e.g., due to small LID isotope enrichment, or due to small pressure increase because of the gas heating by powerful separation laser.

## 4. Results and discussion

Let us start with the discussion of characteristics of the LID effect in our experiment. LID has produced a relatively small change of the *ortho*-to-*para*
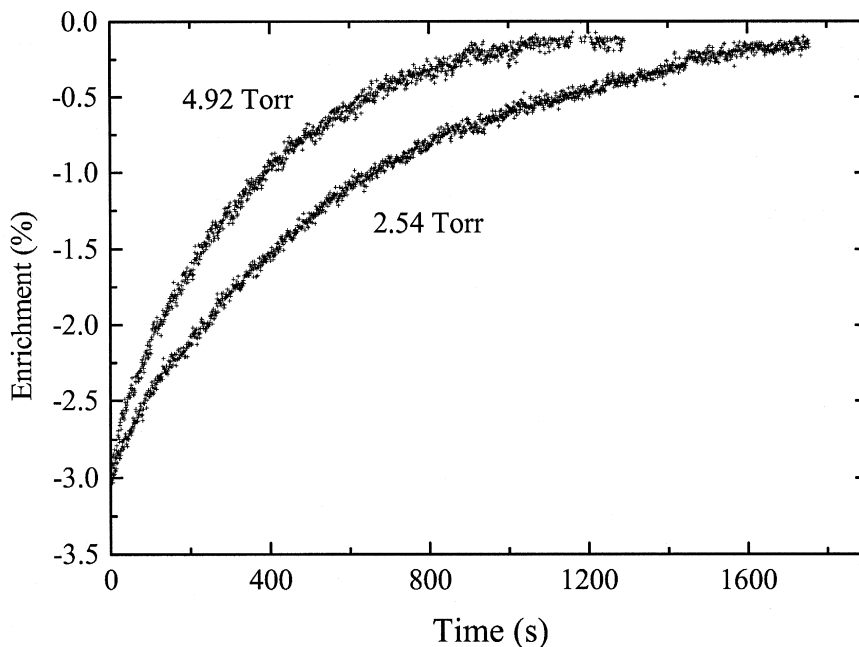


Fig. 2. Examples of the decay curves. The LID effect produces a depletion of the *para* $^{13}C^{12}CH_4$ isomers.
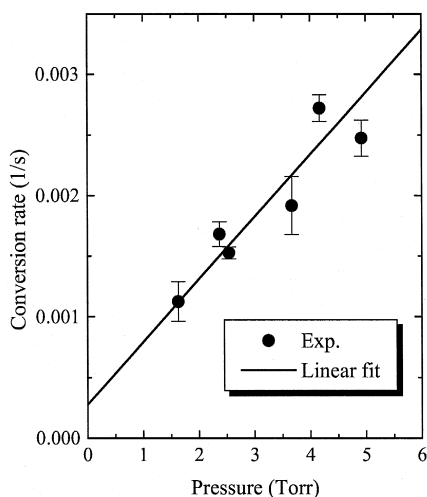
Fig. 3. Pressure dependence of the conversion rate of the $^{13}C^{12}CH_4$ spin isomers.

ratio of ethylene isomers. Although the LID effect in molecular systems is never large, an extra decrease of the LID efficiency in our case was caused by not optimal absorbing-to-buffer particle concentration ratio which was $6/10$ in our case (*para*-to-*ortho* isomer ratio). Note that the largest LID enrichment takes place for a low concentration of absorbing particles diluted in a big amount of buffer particles. A depletion of the concentration of the absorbing spin isomer in our experimental arrangement (see Fig. 1) corresponds to an *increase* of the molecular collision rate upon excitation. Preliminary estimation of the relative change of the ethylene collision rate gives 0.1–0.2%.

Conversion rates of the $^{13}C^{12}CH_4$ spin isomers were measured at a few gas pressures. For each pressure 4 or 3 decay curves were recorded. The conversion rate as a function of the gas pressure is presented in Fig. 3. The data fit well by the linear pressure dependence

$$\gamma = (5.2 \pm 0.8) \cdot 10^{-4} \cdot P + (3 \pm 3) \cdot 10^{-4} \text{ s}^{-1},$$
(1)

where $P$ is the gas pressure in Torr. This rate of isomer conversion appears to be close to the case of the $^{12}CH_3F$ isomers while conversion of the $^{13}CH_3F$ spin isomers is $\simeq 25$ times faster [20,15]. The pressure independent term in Eq. (1) represents the wall contribution to the conversion rate.

Linear pressure dependence of the conversion rate suggests that the possible mechanism is an intramolecular mixing of *ortho* and *para* states. This mechanism was established to be responsible for the isomer conversion in the $CH_3F$ molecules (for the review, see [15]). There is also indication of similar process in the case of formaldehyde ($CH_2O$) [21].

## 5. Conclusions

We have performed the first enrichment of the nuclear spin isomers of ethylene molecules, $^{13}C^{12}CH_4$. The conversion rate was found to be in the '1 hour' range at the gas pressure equal 1 Torr.

Measurements of the pressure dependence have revealed a linear increase of the conversion rate versus the gas pressure. It gave an indication that the conversion of $^{13}C^{12}CH_4$ isomers is governed by the quantum relaxation similar to the $CH_3F$ spin isomers.

## References

[1] A. Farkas, Orthohydrogen, Parahydrogen and Heavy Hydrogen, Cambridge University Press, London, 1935.
[2] M. Quack, Mol. Phys. 34 (1977) 477.
[3] D. Uy, M. Cordonnier, T. Oka, Phys. Rev. Lett. 78 (1997) 3844.
[4] C.R. Bowers, D.P. Weitekamp, Phys. Rev. Lett. 57 (1986) 2645.
[5] J. Bargon, J. Kandels, K. Woelk, Z. Phys. Chem. 180 (1993) 65.

[6] K.F. Bonhoeffer, P. Harteck, Die Naturwiss. 17 (1929) 182.

[7] L.N. Krasnoperov, V.N. Panfilov, V.P. Strunin, P.L. Chapovsky, Pis'ma Zh. Eksp. Teor. Fiz. 39 (1984) 122 [JETP Lett. 39 (1984) 143].

[8] V.K. Konyukhov, A.M. Prokhorov, V.I. Tikhonov, V.N. Faǐzulaev, Pis'ma Zh. Eksp. Teor. Fiz. 43 (1986) 65, [JETP Lett. 43 (1986) 65].

[9] J. Kern, H. Schwahn, B. Schramm, Chem. Phys. Lett. 154 (1989) 292.

[10] R.A. Bernheim, C. He, J. Chem. Phys. 92 (1990) 5959.

[11] C.H. Townes, A.L. Shawlow, Microwave Spectroscopy, Mc-Graw-Hill, New York, 1955.

[12] W.L. Smith, I.M. Mills, J. Chem. Phys. 40 (1964) 2095.

[13] M.D. Vleeschouwer, C. Lambeau, A. Fayt, C. Meyer, J. Mol. Spectrosc. 93 (1982) 405.

[14] A. Fayt, private communication, 1999.

[15] P.L. Chapovsky, L.J.F. Hermans, Annu. Rev. Phys. Chem. 50 (1999) 315.

[16] F.K. Gel'mukhanov, A.M. Shalagin, Pis'ma Zh. Eksp. Teor. Fiz. 29 (1979) 773 [JETP Lett. 29 (1979) 711].

[17] G.J. van der Meer, J. Smeets, S.P. Pod'yachev, L.J.F. Hermans, Phys. Rev. A 45 (1992) 1303.

[18] P.L. Chapovsky, G.J. van der Meer, J. Smeets, L.J.F. Hermans, Phys. Rev. A 45 (1992) 8011.

[19] B. Nagels, P.L. Chapovsky, L.J.F. Hermans, G.J. van der Meer, A.M. Shalagin, Phys. Rev. A 53 (1996) 4305.

[20] P.L. Chapovsky, Zh. Eksp. Teor. Fiz. 97 (1990) 1585 [Sov. Phys. JETP 70 (1990) 895].

[21] G. Peters, B. Schramm, Chem. Phys. Lett. 302 (1999) 181.