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A FTIR polarization spectroscopic investigation

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*Published in:*  
Chemical Physics Letters

*DOI:*  
[10.1016/j.cplett.2018.12.010](https://doi.org/10.1016/j.cplett.2018.12.010)

*Publication date:*  
2019

*Document Version*  
Peer reviewed version

*Citation for published version (APA):*

Nguyen, H. T., Nguyen, D. D., & Spanget-Larsen, J. (2019). Ionic reaction products of iodine with pyridine, 4-methylpyridine, and 4-*tert*-butylpyridine in a polyethylene matrix: A FTIR polarization spectroscopic investigation. *Chemical Physics Letters*, 716, 119-125. <https://doi.org/10.1016/j.cplett.2018.12.010>

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Research paper

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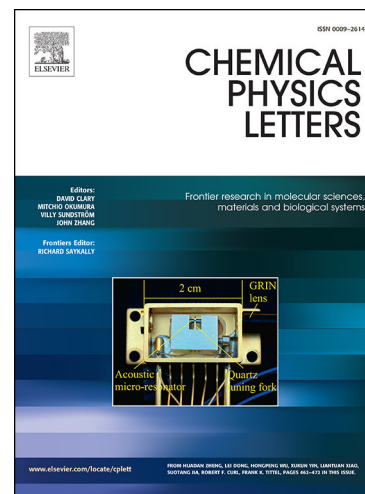
PII: S0009-2614(18)31004-2  
DOI: <https://doi.org/10.1016/j.cplett.2018.12.010>  
Reference: CPLETT 36144

To appear in: *Chemical Physics Letters*

Received Date: 26 September 2018  
Revised Date: 1 December 2018  
Accepted Date: 4 December 2018

Please cite this article as: H. Thu Nguyen, D. Duc Nguyen, J. Spanget-Larsen, Ionic reaction products of iodine with pyridine, 4-methylpyridine, and 4-*tert*-butylpyridine in a polyethylene matrix. A FTIR polarization spectroscopic investigation, *Chemical Physics Letters* (2018), doi: <https://doi.org/10.1016/j.cplett.2018.12.010>

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**Ionic reaction products of iodine with pyridine, 4-methylpyridine, and 4-*tert*-butylpyridine in a polyethylene matrix. A FTIR polarization spectroscopic investigation.**

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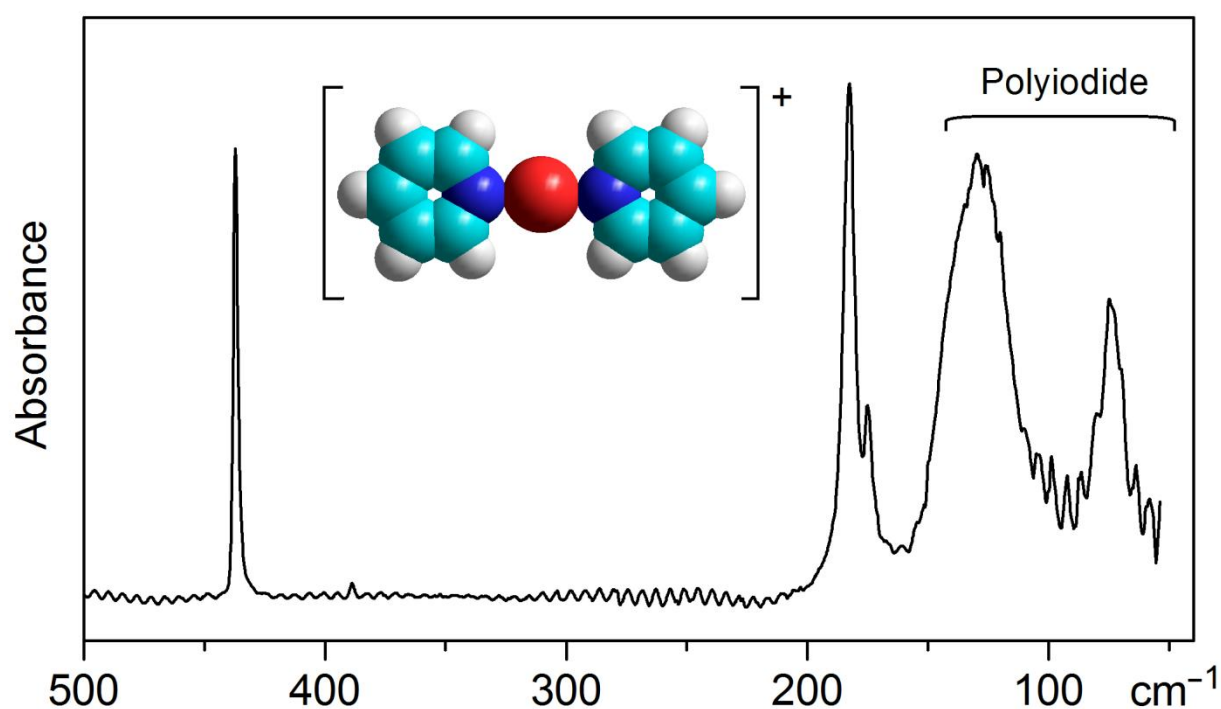
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**KEYWORDS**

bis(pyridine)iodine(I) cation; bis(4-methylpyridine)iodine(I) cation; bis(*t*-butylpyridine)iodine(I) cation; 4-methylpyridinium cation; polyiodide; IR polarization spectroscopy; stretched low-density polyethylene; micro-crystalline aggregates.

**ABSTRACT**

The ionic reaction products of the title pyridines with iodine in low-density polyethylene are identified by comparison of their IR spectra with literature data. The bis(pyridine)iodine(I), bis(4-methylpyridine)iodine(I), and bis(*tert*-butylpyridine)iodine(I) cations are spontaneously formed in the polymer medium. At elevated temperature, the 4-methylpyridinium cation is identified as a product of the reaction between 4-methylpyridine and iodine. In spite of their elongated molecular shape, the bis(pyridine)iodine(I) and bis(4-methylpyridine)iodine(I) cations are randomly aligned in stretched polyethylene; they probably form micro-crystalline polyiodide aggregates in the amorphous regions of the polymer. In contrast, the bis(*tert*-butylpyridine)iodine(I) cation is efficiently aligned in stretched polyethylene.



(Graphical abstract)

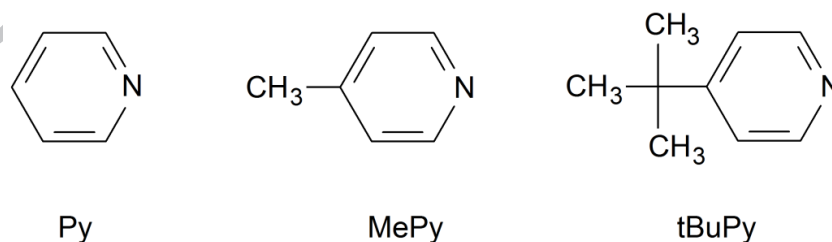
#### Highlights:

- Spontaneous formation of polyiodide salts in low-density polyethylene
- Vibrational fundamentals of the bis(pyridine)iodine(I) cation
- Bis(4-methylpyridine)iodine(I) and bis(*t*-butylpyridine)iodine(I) cations
- Formation of the 4-methylpyridinium cation at elevated temperature
- Possible formation of micro-crystalline polyiodide aggregates in polyethylene

## 1. Introduction

It is well known that pyridine and other aza-aromatics may react with diiodine to form so-called charge transfer (CT) complexes [1]. This is a classic example of the non-covalent interaction designated as halogen bonding [2,3]. In general, the 1:1 pyridine-diiodine CT complex is stable in ‘inert’ media, while ionic compounds are formed in ionizing media [4,5]. But some years ago it was discovered that the reaction between pyridine and diiodine dissolved in low-density polyethylene (PE) leads to ionic species as the main products, corresponding to a polyiodide salt [6]. The spontaneous and efficient formation of charged solute species in an alkane medium like PE was surprising. Ionic reaction products of pyridine with diiodine had not previously been observed in an alkane environment [4]. Evidently, the conditions prevailing in the reaction cavities of a PE host somehow catalyze the formation of ionic products.

The ionic product of the reaction between pyridine and diiodine in PE was first assigned to *N*-iodopyridinium polyiodide [6]. In the present communication we reconsider the reaction, arriving at a different assignment of the ionic product. We furthermore extend the investigation to the corresponding systems involving 4-methylpyridine ( $\gamma$ -picoline) and 4-*tert*-butylpyridine (Scheme 1). The 4-*tert*-butylpyridine/iodine system is of particular interest because of its possible importance in dye-sensitized solar cells [7-11]. The reaction between the pyridines and diiodine, confined to the cavities of a stretched PE host, is investigated by Fourier Transform Infrared (FTIR) Linear Dichroism (LD) spectroscopy [12-16]. The observed LD contains information on the vibrational transition moment directions [12-16] of the product species, thereby providing a clue to their structural assignment. The study is supported by the results of quantum chemical calculations. Additional information is provided as supplementary data, referred to as S1–S10 in the ensuing text.



**Scheme 1.** Pyridine (Py), 4-methylpyridine (MePy), and 4-*tert*-butylpyridine (tBuPy).

## 2. Calculations

Quantum chemical calculations on the parent bis(pyridine)iodine(I) cation,  $\text{Py}_2\text{I}^+$ , were performed with the GAUSSIAN09 software package [17] by using B3LYP [18,19] density functional

theory (DFT) and the LanL2DZ [20,21] basis set. Vibrational transitions were computed within the harmonic approximation and by using the anharmonic second order perturbation (VPT2) procedure by Barone and coworkers (freq=anharm) [22-24]. The predicted nuclear equilibrium coordinates and fundamental vibrational transitions are provided as S1. The computed anharmonic wavenumbers are essentially proportional to the harmonic values ( $\nu_{\text{anharm}} = 0.96629 \times \nu_{\text{harm}}$ ;  $R = 0.9999$ ,  $SD = 17.9 \text{ cm}^{-1}$ ). The suggested assignment of the observed transitions to the calculated ones is given in Table 1.

### 3. Experimental

Pyridine (Py), 4-methylpyridine (MePy), and diiodine ( $\text{I}_2$ ) were purchased from Aldrich (+99%), 4-*tert*-butylpyridine (tBuPy) from Fluka (98%), solvents  $\text{CCl}_4$ ,  $\text{CS}_2$ , and methanol from Merck (Uvasol). Polyethylene (PE) material was obtained from laboratory bottles of low-density PE (Kartell Art. 1616).

Ca.  $2.5 \times 5 \text{ cm}$  PE pieces cut from the bottles were heated between aluminum plates at  $140^\circ\text{C}$  for 30 minutes, quenched in cold water, and uniaxially stretched by approximately 500%. Before stretching, the thickness of the PE was 1.2 mm, after stretching 0.45 mm. According to Differential Scanning Calorimetry (DSC) analyses, the stretching increased the crystallinity of the polymer from ca. 23% to ca. 37% (S2).

Stretched PE samples saturated with Py, MePy, or tBuPy were obtained by submersion in the liquid substance in a sealed container at  $50^\circ\text{C}$  for 24 hours. The surfaces of the doped samples were washed with methanol to remove residual pyridine. No noticeable relaxation of the samples as a result of the doping process was observed. The mass increase of a saturated, dried sample was in the range 2.0 – 2.5% (S3). Each sample was then placed in a sealed reaction container with iodine crystals, allowing iodine to enter the polymer by sublimation; the additional mass-increase due to accumulation of iodine was 8 – 9% (S4). The samples were prepared in air. No effects due to reaction with oxygen were observed. The final samples were “black” and opaque in the UV-vis region (S4). For the use as references, stretched samples without solutes were produced in the same manner.

The reaction experiments were conducted at different temperatures: 0, 22, 30, 40, and  $50^\circ\text{C}$ . The progression of the reactions was followed by measuring the IR spectra of the samples at different reaction times, ranging from hours to days. Before each measurement, the surface of the samples was washed with methanol to remove deposits. However, experiments conducted at elevated temperatures for several days frequently affected the properties of the PE polymer, thereby complicating analysis of the recorded spectra. Finally, volatile solutes were allowed to evaporate

from the sample and their IR spectra were recorded. The evaporation rates of Py, MePy, or tBuPy solutes from the stretched PE material at room temperature were determined in an independent series of experiments, see S3.

IR spectra were measured on a Perkin-Elmer Spectrum 2000 FTIR spectrophotometer equipped with a rotatable KRS5 aluminum grid polarizer in the sample beam as previously described [6]. The spectra were recorded with a spectral resolution of  $1\text{ cm}^{-1}$  and 10 scans. Because of strong baseline absorption, the region  $3000\text{-}2700\text{ cm}^{-1}$  and three narrow regions around  $1460$ ,  $1365$ , and  $720\text{ cm}^{-1}$  could not be measured. Two linearly independent absorbance curves were recorded on the stretched PE samples, one with the polarization of the beam parallel to the stretching direction ( $U$ ), and another with the polarization perpendicular to it ( $V$ ). The resulting baseline corrected LD absorbance curves are denoted  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$ . The corresponding isotropic absorbance curve for an uniaxial sample is given by  $E_{\text{ISO}}(\tilde{\nu}) = (E_U(\tilde{\nu}) + 2 E_V(\tilde{\nu}))/3$  [12-16].

#### 4. Orientation factors.

The directional information that can be extracted from the LD curves is represented by the orientation factors  $K_i$  for the observed peaks [13,14]:

$$K_i = \langle \cos^2(\mathbf{M}_i, U) \rangle$$

Here  $(\mathbf{M}_i, U)$  is the angle between the moment vector  $\mathbf{M}_i$  of the  $i$ 'th transition and the stretching direction  $U$  of the polymer; the pointed brackets indicate averaging over all molecules in the light path. Large  $K$  values correspond to transition moments well aligned with the stretching direction, and vice versa. For an isotropic sample all  $K$  values will be equal to  $1/3$ . The  $K$ s may be determined by the graphical TEM stepwise reduction procedure [13,14] which involves the formation of linear combinations of  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$ , such as the family of reduced absorbance curves  $r_K(\tilde{\nu})$  [25]:

$$r_K(\tilde{\nu}) = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$$

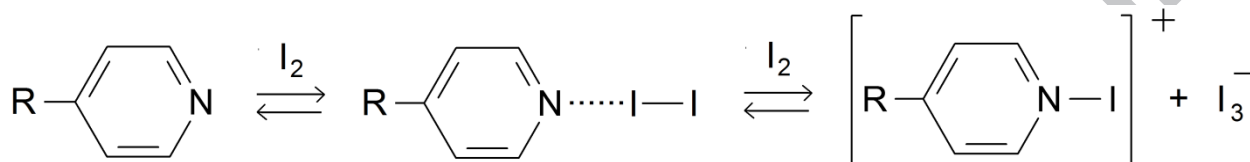
A peak or a shoulder due to transition  $i$  will vanish from the linear combination  $r_K(\tilde{\nu})$  for  $K = K_i$ . The orientation factors  $K_i$  can thus be determined by visual inspection [25], see f. ex. Fig. 1.

### 5. Results and discussion

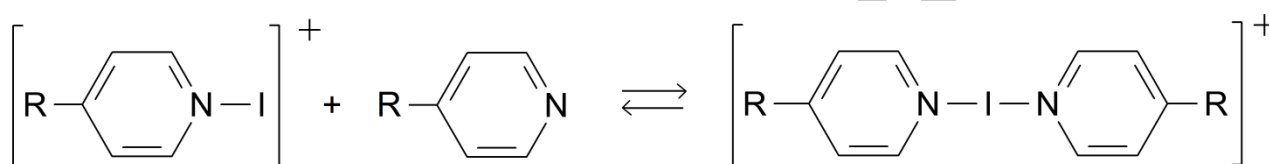
#### 5.1 Pyridine/iodine system

In the previous investigation [6] of the reaction between Py and  $\text{I}_2$  in a polyethylene host, stretched as well as unstretched, the observed ionic product was assigned to *N*-iodopyridinium

polyiodide,  $\text{PyI}^+, \text{I}_x^-$ , assuming the reaction mechanism outlined in Scheme 2 ( $\text{R} = \text{H}$ ). The assignment was based on a comparison of the observed spectrum with a previously published spectrum assigned to the  $\text{PyI}^+$  cation [27]. However, we have come to the conclusion that the observed cation product is the bis(pyridine)iodine(I) cation  $\text{Py}_2\text{I}^+$ , see Scheme 3 ( $\text{R} = \text{H}$ ). As indicated in Table 1, the IR spectrum of the observed ionic product is in excellent agreement with the IR spectrum of the  $\text{Py}_2\text{I}^+$  cation published by Haque and Wood [26].



Scheme 2



Scheme 3.

The bis(pyridine)iodine(I) cation is an interesting species. The tetrafluoroborate,  $\text{Py}_2\text{I}^+, \text{BF}_4^-$ , is an iodinating reagent known as Barluenga's reagent [28,29]. Haque and Wood [26] deduced from studies of the IR and Raman spectra of  $\text{Py}_2\text{I}^+, \text{BF}_4^-$  and  $\text{Py}_2\text{I}^+, \text{PF}_6^-$  in nujol mull and in liquid solutions that the pyridine rings in  $\text{Py}_2\text{I}^+$  are nearly co-planar, a result which is consistent with those of crystal analyses [30-32]. One of the first theoretical studies of the  $\text{Py}_2\text{I}^+$  cation was published by Sabin [33], using semiempirical procedures. More recently, the electronic structures of  $\text{Py}_2\text{I}^+$  and related species were investigated by Georgiou et al. [34], concluding that  $\text{Py}_2\text{I}^+$  can be considered as a coordination complex of  $\text{I}^+$ . The molecular equilibrium structure of  $\text{Py}_2\text{I}^+$  in the gas phase was found to have  $\text{D}_{2d}$  symmetry, with mutually perpendicular pyridine rings, but the barrier to rotation around the N-I-N axis was predicted to be small [34]. With B3LYP/LanL2DZ we compute a difference in electronic energy of  $0.3 \text{ kcal mol}^{-1}$  between the  $\text{D}_{2d}$  and the planar  $\text{D}_{2h}$  conformation in the gas phase.

In Table 1 we list the transitions predicted for  $\text{Py}_2\text{I}^+$  under the assumption of co-planar rings in the condensed phase ( $\text{D}_{2h}$  symmetry). It is apparent that the agreement with the observed spectrum is satisfactory. The transitions observed at  $637$  and  $183 \text{ cm}^{-1}$  (Fig. 2) can be assigned to the vibrational modes  $\nu_{44}(b_{1u})$  and  $\nu_{45}(b_{1u})$  which both involve asymmetric stretching motions of the unique N-I-N moiety of  $\text{Py}_2\text{I}^+$ . The suggested assignments of the main transitions of  $\text{Py}_2\text{I}^+$  to calculated fundamental transitions are listed in Table 1. The complete spectrum comprising more



than 40 observed peaks is provided as S5, with indication of wavenumbers, absorbances, and integrated intensities.

The identification of the cation product as  $\text{Py}_2\text{I}^+$  raises a question: Why is this fairly elongated species not efficiently aligned in stretched PE? The observed orientation factors  $K_i$  for 30 vibrational transitions of  $\text{Py}_2\text{I}^+$  all fall in the range 0.3 – 0.4 [6], corresponding to nearly random alignment. We suggest that the lack of alignment can be explained by the formation of micro-crystalline polyiodide aggregates, probably imbedded in the amorphous regions in the polymer. The suggestion is supported by the following observations:

(1) The results of detailed experimental investigations [36-40] show that solutes in PE are either located in the amorphous regions of the polymer or residing on the surfaces of the PE crystallites; only the latter fraction becomes oriented by stretching of the polymer. The formation of crystalline aggregates in the amorphous regions thus explains why no alignment is observed on stretching. Even interaction of the aggregates with the crystallite surfaces would not necessarily lead to appreciable alignment of the individual  $\text{Py}_2\text{I}^+$  cations. As discussed in the following Section 5.2, similar lack of alignment is observed for  $(\text{MePy})_2\text{I}^+$ , most likely for a similar reason.

(2) As shown in S5, all the observed IR peaks for  $\text{Py}_2\text{I}^+$  in PE are very sharp, much sharper than typical peaks due to Py and  $\text{Py} \cdot \text{I}_2$  (e.g., Fig. 1), indicating minimal inhomogeneous line broadening. Hence, all  $\text{Py}_2\text{I}^+$  species in the PE sample must have very similar environments. Crystalline aggregates provide a well-defined homogenous micro-environment for the  $\text{Py}_2\text{I}^+$  cations, thereby explaining the remarkable sharpness of the bands.

(3) Finally: Analyses of crystalline bis(pyridine)iodine(I) polyiodide characterize the salt as a hepta-iodide, involving the anion  $\text{I}_7^-$  (or  $2\text{I}_2 \cdot \text{I}_3^-$ ) [30,32]. This is consistent with the result of an approximate stoichiometric analysis of the product formed in PE, see S4 for details.

The assumption that pyridine and iodine in PE react to form micro-crystalline  $\text{PyI}^+, \text{I}_x^-$  aggregates is thus supported by a number of observations. But the present spectroscopic evidence does not provide an indication of the size and detailed nature of the possible aggregates. The subject requires further and more advanced investigations, for example like the one published by Wirtz et al. [40].

#### 5.2. 4-Methylpyridine/iodine system

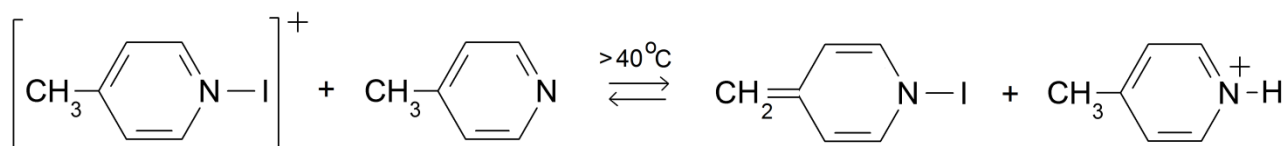
The reaction between MePy and  $\text{I}_2$  has been investigated by several workers [26,41-45]. The charge transfer complex  $\text{MePy} \cdot \text{I}_2$  is readily observed in solvents like  $\text{CCl}_4$  and  $\text{CS}_2$ . The IR bands of MePy and  $\text{MePy} \cdot \text{I}_2$  tend to overlap, but transitions observed close to 1212, 1067, 1009, and  $530 \text{ cm}^{-1}$  in  $\text{CCl}_4$  and  $\text{CS}_2$  solutions can be assigned to  $\text{MePy} \cdot \text{I}_2$  (S6). In ionizing solvents the situation is

more complicated, leading to a variety of products, particularly at elevated temperature (see below) [44,45].

The spectral development of the MePy/iodine system in stretched PE at 22 °C is provided as S7, comprising a series of spectra recorded at different intervals of time. Bands due to  $\text{MePy} \cdot \text{I}_2$  are not easily observed in these spectra, indicating fast further reactions. After one day, the spectrum indicates a mixture of primarily MePy and the bis(4-methylpyridine)iodine(I) cation,  $(\text{MePy})_2\text{I}^+$  (S7, S8). The reaction may proceed according to Schemes 2 and 3 ( $\text{R} = \text{CH}_3$ ), but also other reaction mechanisms have been suggested [44,45]. In Fig. 3, the contributions due to MePy have been subtracted from the spectrum. The prominent peaks in the resulting curve are consistent with the spectrum of the  $(\text{MePy})_2\text{I}^+$  cation derived by Haque and Wood [44] from the spectra of the  $\text{BF}_4^-$  and  $\text{PF}_6^-$  salts. After prolonged reaction time the spectrum is changed (S7), indicating the possible formation of additional reaction products.

The LD absorption curves corresponding to the isotropic spectrum in Fig. 3 are shown in S8 (without subtraction of contributions from MePy). The peaks assigned to  $(\text{MePy})_2\text{I}^+$  have orientation factors  $K$  between 0.3 and 0.4, corresponding to essentially random orientation. This is not what one would normally expect for an elongated species like  $(\text{MePy})_2\text{I}^+$  in stretched PE. A possible explanation would be the formation of polyiodide aggregates, similar to the situation discussed for  $\text{Py}_2\text{I}^+$  (Section 5.1).

According to Bora, Hass and Haque [45] the kinetics of the reaction between MePy and  $\text{I}_2$  in a polar solvent changes at elevated temperatures. Above 38 °C and with excess MePy, the reaction proceeds to a variety of products, including the methylpyridinium cation ( $\text{MePyH}^+$ ) and cations like  $\text{MePy-CH}_2\text{-Py}^+$ ,  $\text{MePy-CH}_2\text{-Py-CH}_2\text{-Py}^{2+}$ , etc. [44,45]. Fig. 4 shows the spectrum observed after one day in stretched PE at 50 °C. The strong, broad band system with maxima at 3250, 3167, and 3083  $\text{cm}^{-1}$  (and Evans windows at 3195 and 3123  $\text{cm}^{-1}$ ) may be due to the N–H stretching vibration of  $\text{MePyH}^+$ . In fact, the spectrum in Fig. 4 is consistent with the spectrum of 4-methylpyridinium perchlorate ( $\text{MePyH}^+, \text{ClO}_4^-$ ) in acetonitrile solution published by Brzezinski and Zundel [46]. The peaks close to 3250, 3167, 3083, 1637, 1599, 1505, 1311, and 1244  $\text{cm}^{-1}$  are thus found in both spectra. At lower wavenumbers, the spectrum published by Brzezinski and Zundel [46] shows strong bands due to the perchlorate ion. The proton in  $\text{MePyH}^+$  may be donated from the methyl group in  $\text{MePyI}^+$ , as indicated in Scheme 4, or perhaps more likely from  $(\text{MePy})_2\text{I}^+$  as suggested by Haque and coworkers [44,45].



**Scheme 4.** Possible proton transfer from 4-methyl-*N*-iodopyridinium (MePyI<sup>+</sup>) to 4-methylpyridine (MePy) to yield 4-methylidene-*N*-iodopyridine and 4-methylpyridinium (MePyH<sup>+</sup>).

### 5.3. 4-*tert*-Butylpyridine/iodine system

The spectroscopic properties of this system were recently investigated in some detail by Hansen et al. [11]. The IR spectrum of the solid, red substance isolated from a solution of tBuPy and I<sub>2</sub> in methanol showed that the product was a mixture of the CT complex tBuPy·I<sub>2</sub> and bis(4-*tert*-butylpyridine)iodine(I) triiodide, (tBuPy)<sub>2</sub>I<sup>+</sup>,I<sub>3</sub><sup>-</sup>. Analysis of the observed spectrum in terms of contributions from the two components was complicated by near-coincidence of bands, but the results of quantum chemical calculations enabled assignment of all significant transitions in the 1600 – 400 cm<sup>-1</sup> region [11].

The formation of tBuPy·I<sub>2</sub> is observed in CCl<sub>4</sub> and CS<sub>2</sub> solutions, but the IR bands of tBuPy and tBuPy·I<sub>2</sub> overlap strongly, and only a well-resolved peak at 1011 cm<sup>-1</sup> is easily assigned to tBuPy·I<sub>2</sub> (S9). In the solid state this transition is observed at 1013 cm<sup>-1</sup> and additional peaks at 1548, 1415, 1216, 1069, 828, and 723 cm<sup>-1</sup> were assigned to tBuPy·I<sub>2</sub> [11]. The transition at 1011 cm<sup>-1</sup> is observed after a few minutes in stretched PE at 22 °C (S8), and it remains as a weak feature in the spectra recorded after longer reaction times.

After one day (S10), the observed spectrum indicate a mixture of tBuPy, tBuPy·I<sub>2</sub>, and the (tBuPy)<sub>2</sub>I<sup>+</sup> cation. Fig. 5 shows a portion of the corresponding LD absorption curves. The (tBuPy)<sub>2</sub>I<sup>+</sup> cation appears to be well-aligned in stretched PE. Very large orientation factors are determined for the peaks at 1217, 1061, 1021, and 543 cm<sup>-1</sup>, amounting to  $K = 0.9$ . These transitions must be assigned to long-axis polarized transitions in the (tBuPy)<sub>2</sub>I<sup>+</sup> cation. The corresponding peaks in the solid state spectrum of (tBuPy)<sub>2</sub>I<sup>+</sup>,I<sub>3</sub><sup>-</sup> are observed at 1216, 1061, 1021, and 543 cm<sup>-1</sup> [11]. A small  $K$  value around 0.1 is observed for the peak at 843 cm<sup>-1</sup>, indicating a short-axis polarized transition in (tBuPy)<sub>2</sub>I<sup>+</sup>; this peak is observed at 833 cm<sup>-1</sup> in the solid state [11]. The orientation factors for the transitions assigned to unreacted tBuPy all fall in the approximate range  $K = 0.3 - 0.4$ , corresponding to nearly random orientation in stretched PE. The peak at 1011 cm<sup>-1</sup> has  $K$  between 0.6 and 0.7, consistent with assignment to a long-axis polarized transition in the complex tBuPy·I<sub>2</sub>.

The orientation factors observed for the (tBuPy)<sub>2</sub>I<sup>+</sup> cation shows that it is aligned like a “normal” elongated, rod-like molecule in stretched PE. This is in marked contrast to the lack of

alignment observed for the  $\text{Py}_2\text{I}^+$  and  $(\text{MePy})_2\text{I}^+$  cations, an observation which can possibly be explained by aggregation as discussed above (Sections 5.1 and 5.2).

## 6. Conclusions

The reaction of pyridine (Py), 4-methylpyridine (MePy), and 4-*tert*-butylpyridine (tBuPy) with iodine in a low-density polyethylene (PE) matrix at room temperature leads to the formation of  $\text{Py}_2\text{I}^+$ ,  $(\text{MePy})_2\text{I}^+$ ,  $(\text{tBuPy})_2\text{I}^+$  cations, respectively. At elevated temperature, the 4-methylpyridinium cation ( $\text{MePyH}^+$ ) was observed in the case of MePy. The identification of the observed cations was based on comparison of their IR spectra with spectra from the literature. In addition, the vibrational transitions observed for  $\text{Py}_2\text{I}^+$  were consistent with theoretically predicted transitions. In spite of their elongated molecular shape, the  $\text{Py}_2\text{I}^+$  and  $(\text{MePy})_2\text{I}^+$  cations are almost randomly aligned in stretched PE. This is most likely due to formation of micro-crystalline polyiodide aggregates in the amorphous regions of the polymer. In contrast,  $(\text{tBuPy})_2\text{I}^+$  is very efficiently aligned, with an orientation factor for the long molecular axis equal to  $K = 0.9$ ; this may indicate that no significant aggregation occurs in this case. The present spectroscopic evidence does not explain the origin of the different behavior of  $\text{Py}_2\text{I}^+$  and  $(\text{MePy})_2\text{I}^+$  relative to that of  $(\text{tBuPy})_2\text{I}^+$ . Full elucidation of these phenomena requires further investigations.

## Acknowledgements

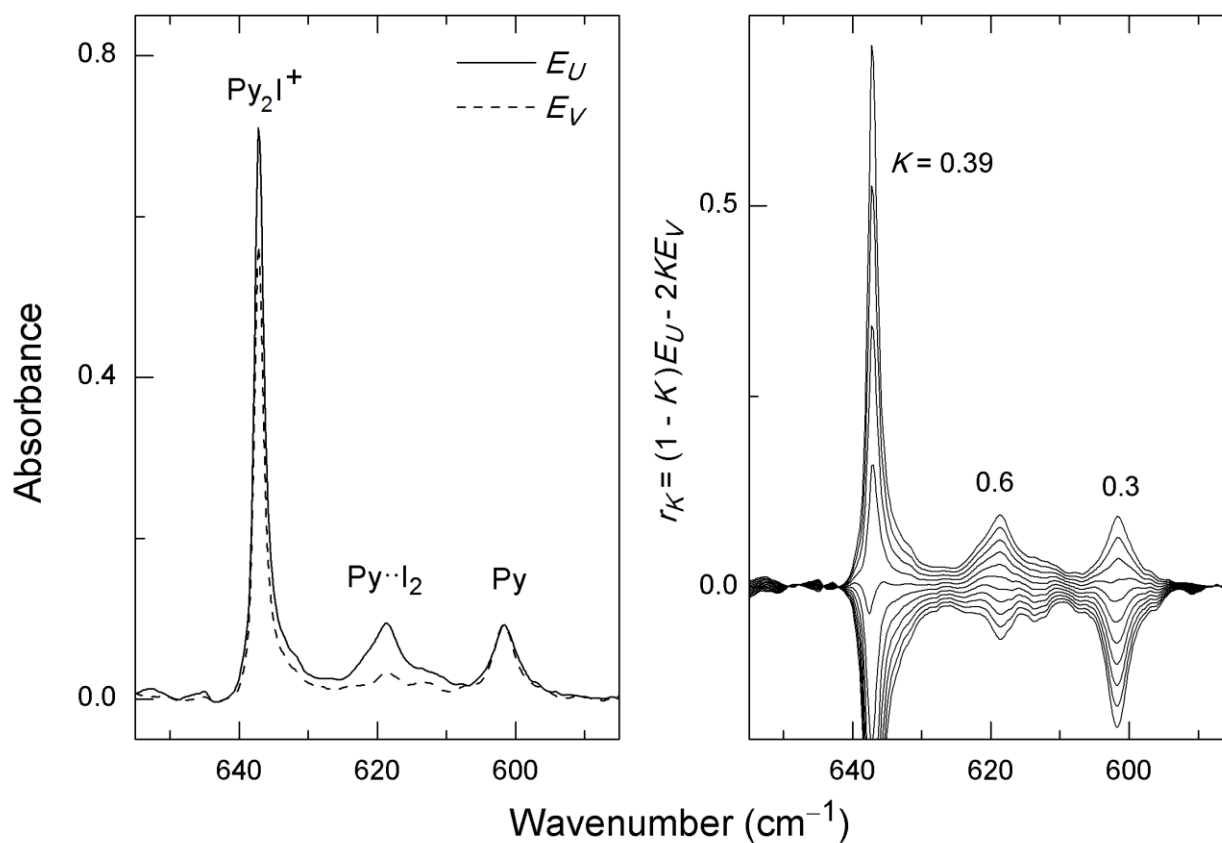
The stay of Nguyen Thu Huong at Roskilde University was part of an Enhancement of Research Capacity (ENRECA) program funded by the Danish International Development Agency (DANIDA). The stay of Nguyen Duc Duy at Roskilde University was enabled by a Ph.D. scholarship granted by the Vietnamese Ministry of Education and Training; additional support was provided by the ENRECA program. The authors are grateful to Cuong Hoang Ngoc for performing the Differential Scanning Calorimetry (DSC) measurements, to Eva M. Karlsen for technical assistance in the spectroscopy lab, and to Peter W. Thulstrup and Søren Hvidt for helpful discussions.

**Table 1**IR transitions for the bis(pyridine)iodine(I) cation,  $\text{Py}_2\text{I}^+$ .

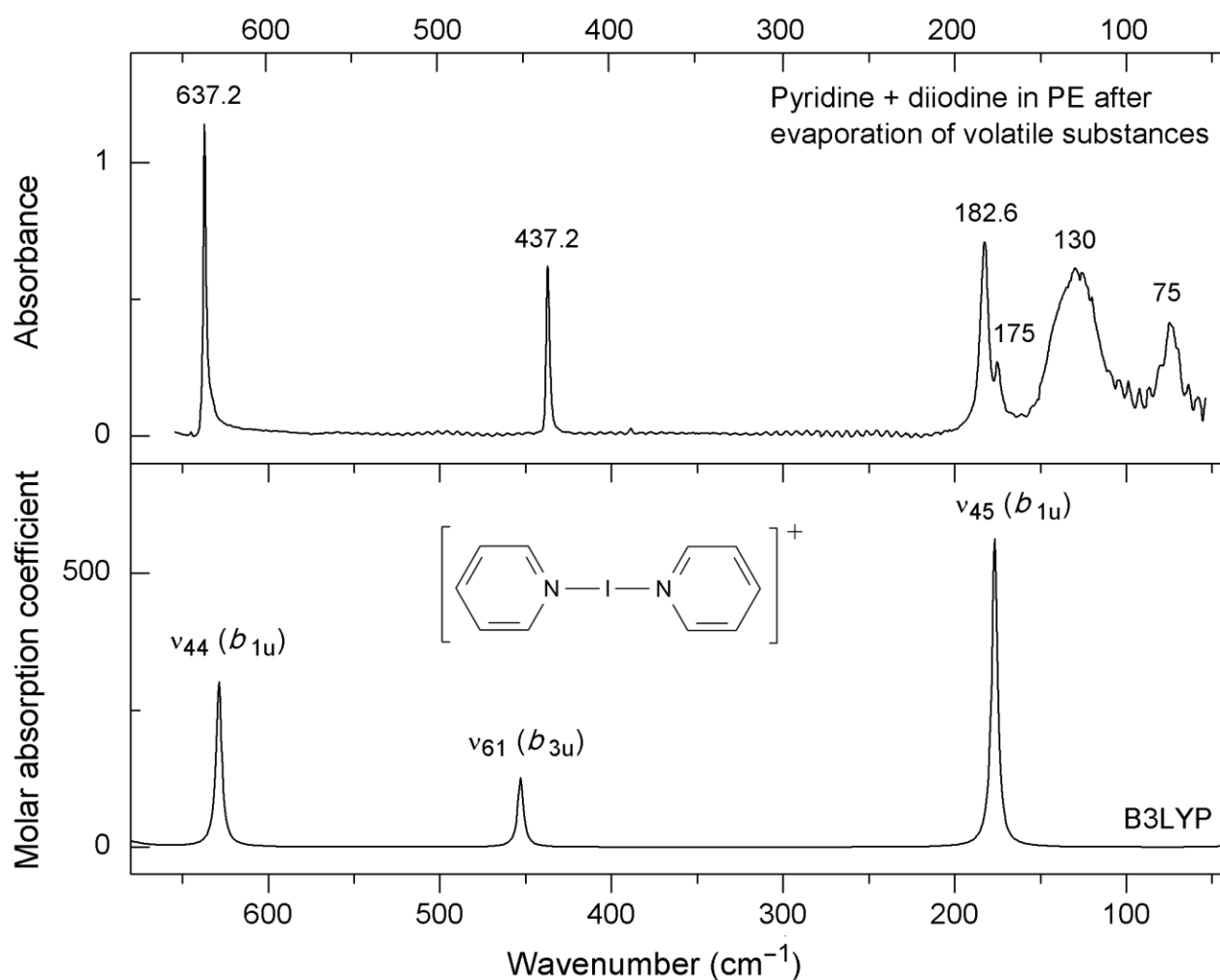
$\text{Py}_2\text{I}^{+ a}$	$\text{Py}_2\text{I}^+, \text{I}_x^{- b}$		B3LYP/LanL2DZ (D <sub>2h</sub> symmetry) <sup>c</sup>				
$\tilde{\nu}^{d,e}$	$\tilde{\nu}^d$	$E_{\text{ISO}}^f$	$\tilde{\nu}^{d,g}$			$I^h$	App. description <sup>i</sup>
1602 s	1599.0	98	$\nu_{38}$	$b_{1u}$	1586	66	Py skel def + CH b
	1588.2	4					
1576 w	1570.4	12	$\nu_{48}$	$b_{2u}$	1560	3	Py skel def
1481 w			$\nu_{39}$	$b_{1u}$	1458	6	Py skel def + CH b
1452 s			$\nu_{49}$	$b_{2u}$	1437	141	Py skel def + CH b
~1400 w	1394.0	16					
1355 m	1348.0	33	$\nu_{50}$	$b_{2u}$	1350	5	CH b
	(1331)						
1246 m	1251.4	54	$\nu_{51}$	$b_{2u}$	1285	4	Py skel def
1210 s	1202.8	47	$\nu_{40}$	$b_{1u}$	1208	56	CH b
	(1190)						
1158 s	1155.2	12	$\nu_{52}$	$b_{2u}$	1171	5	CH b
1090 w	1089.6	8					
1062 s	1058.6	100	$\nu_{41}$	$b_{1u}$	1048	100	Py skel def + CH b
1040 m	1038.0	37	$\nu_{42}$	$b_{1u}$	1020	17	Py skel def
1009 s	1008.6	102	$\nu_{43}$	$b_{1u}$	982	141	Py ring breath
1005 w	(1004)						
	976.0	7					
945 w	944.0	8	$\nu_{58}$	$b_{3u}$	957	3	CH oop b
	871.2	4					
	(777)						
760 s	754.8	201	$\nu_{59}$	$b_{3u}$	771	142	CH oop b
707 m	699.4	25					
692 s	688.2	261	$\nu_{60}$	$b_{3u}$	698	182	CH oop b
	676.6	48					
637 s	637.2	75	$\nu_{44}$	$b_{1u}$	629	57	Py skel def, N–I–N
438 s	437.2	40	$\nu_{61}$	$b_{3u}$	453	24	Py skel oop def
	388.8	3	$\nu_{33}^?$	$a_u$	389	0	Py skel oop def
172 s	182.6	109	$\nu_{45}$	$b_{1u}$	177	107	N–I–N s (asym)
	175.2	39	$\nu_{11}^?$	$a_g$	159	0	N–I–N s (sym)
	130 <sup>j</sup>	433					
	75 <sup>j</sup>	157					

 $^a$  Derived from spectra of  $\text{Py}_2\text{I}^+, \text{BF}_4^-$  and  $\text{Py}_2\text{I}^+, \text{PF}_6^-$  in  $\text{CH}_2\text{Cl}_2$  (1650–400  $\text{cm}^{-1}$ ) and pyridine (400–150  $\text{cm}^{-1}$ ) [26]. $^b$   $\text{Py}_2\text{I}^+, \text{I}_x^-$  in stretched low-density polyethylene (PE) [6]. Further details are given in S5. $^c$  Harmonic fundamentals in the gas phase. Full listing provided as S1. $^d$  Wavenumbers in  $\text{cm}^{-1}$ . $^e$  s = strong, m = medium, w = weak. $^f$  Integrated intensity  $E_{\text{ISO}} = E_U + 2E_V$  relative to  $E_{\text{ISO}}(1058.6 \text{ cm}^{-1}) = 100$ . $^g$  Scaling factor  $\alpha = 0.9663$ . $^h$  Calculated IR intensity relative to  $I(\nu_{41}) = 100$ . $^i$  s = stretching, b = bending, oop = out-of-plane, skel = skeleton, def = deformation. $^j$  Polyiodide band.

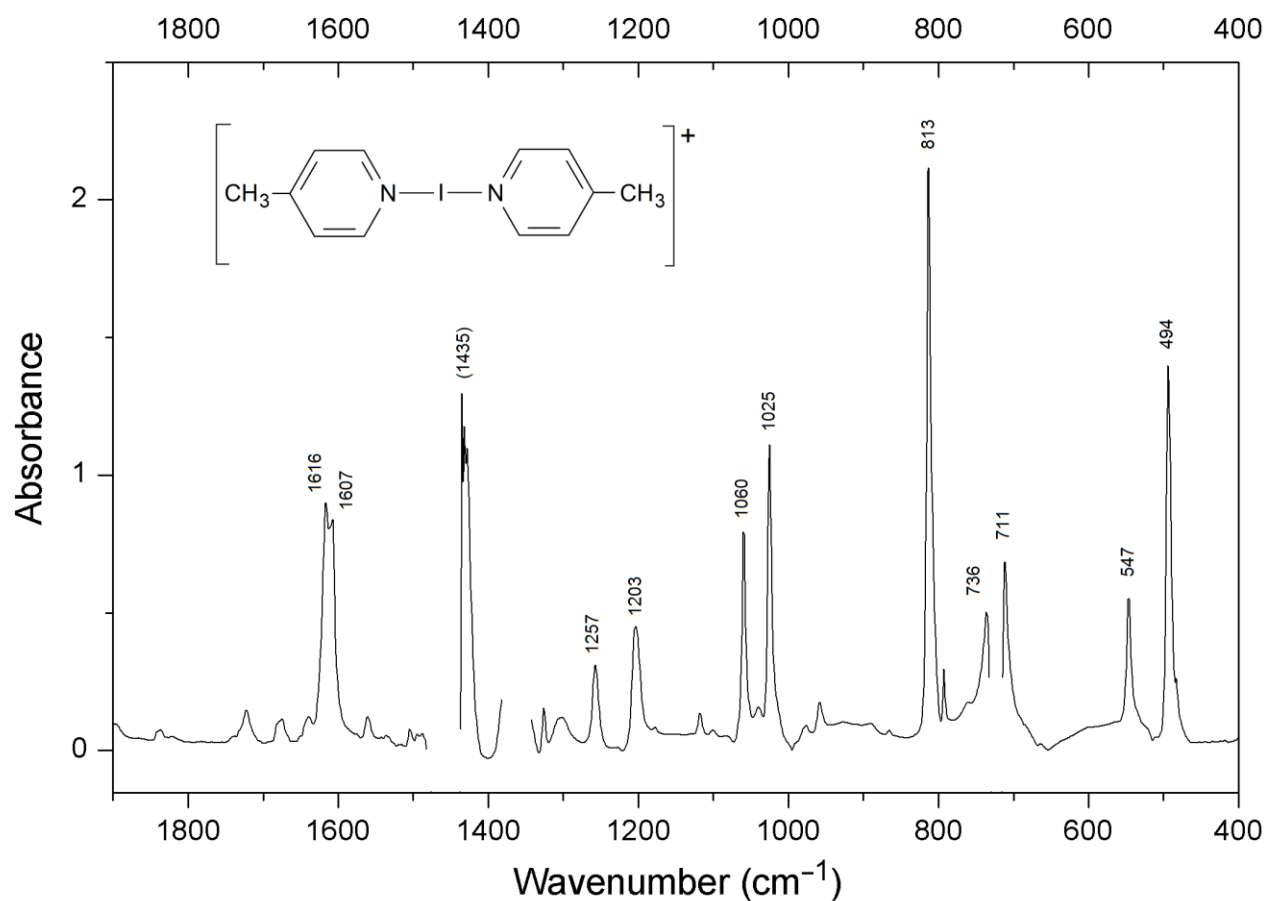
## Figures and schemes



**Figure 1.** *Left:* Linear dichroic (LD) absorption curves in the 650-590  $\text{cm}^{-1}$  region for the pyridine/iodine system in stretched polyethylene at room temperature.  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$  designate the absorbance measured with light polarized parallel ( $U$ ) and perpendicular ( $V$ ) to the stretching direction. *Right:* Family of reduced absorption curves  $r_K(\tilde{\nu}) = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$  for orientation factors  $K$  ranging from 0 to 1. The resulting  $K$  values are indicated (see text).

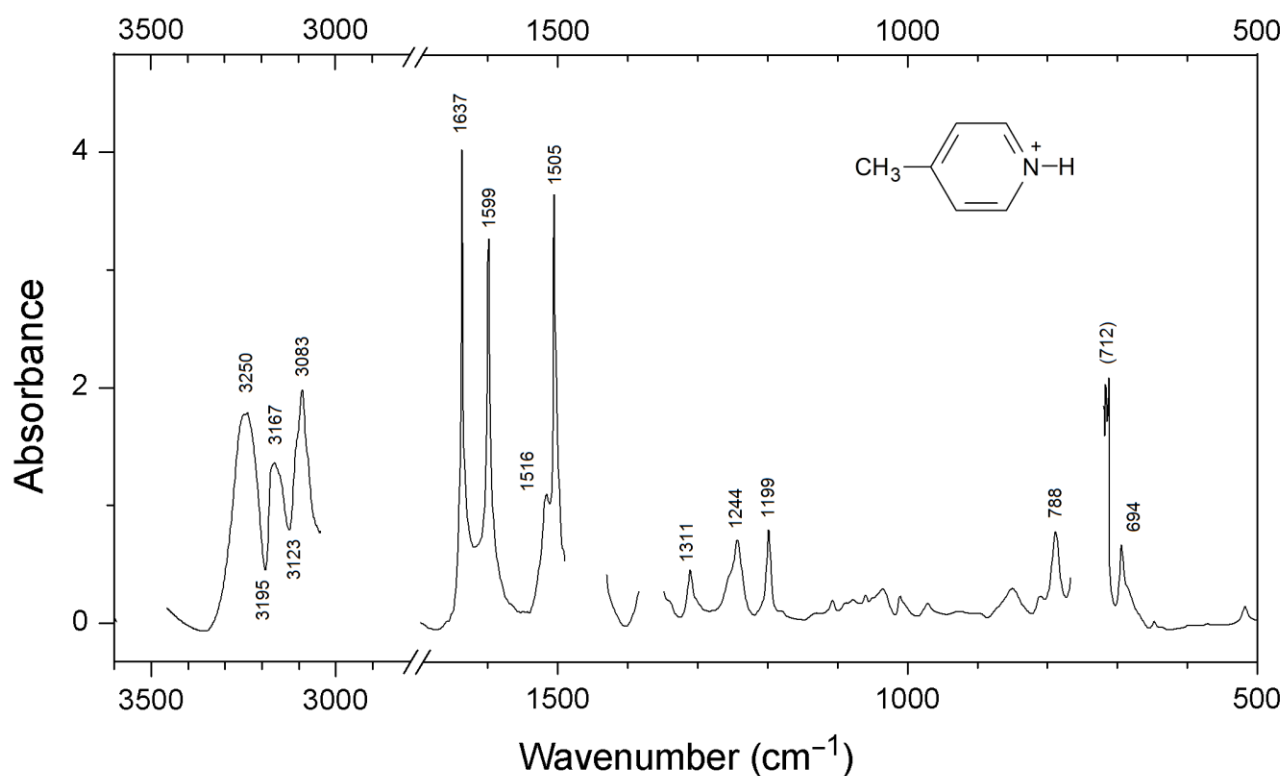


**Figure 2.** *Top:* Observed isotropic IR spectrum of the pyridine/iodine system in stretched polyethylene after evaporation of volatile substances [6]. *Bottom:* Calculated absorbance spectrum of the bis(pyridine)iodine(I) cation,  $\text{Py}_2\text{I}^+$ , under the assumption of planar  $D_{2h}$  symmetry (Table 1). The molar absorption coefficient was estimated under the assumption of Lorentz band shapes with full width at half maximum (FWHM) equal to  $4 \text{ cm}^{-1}$  [35].

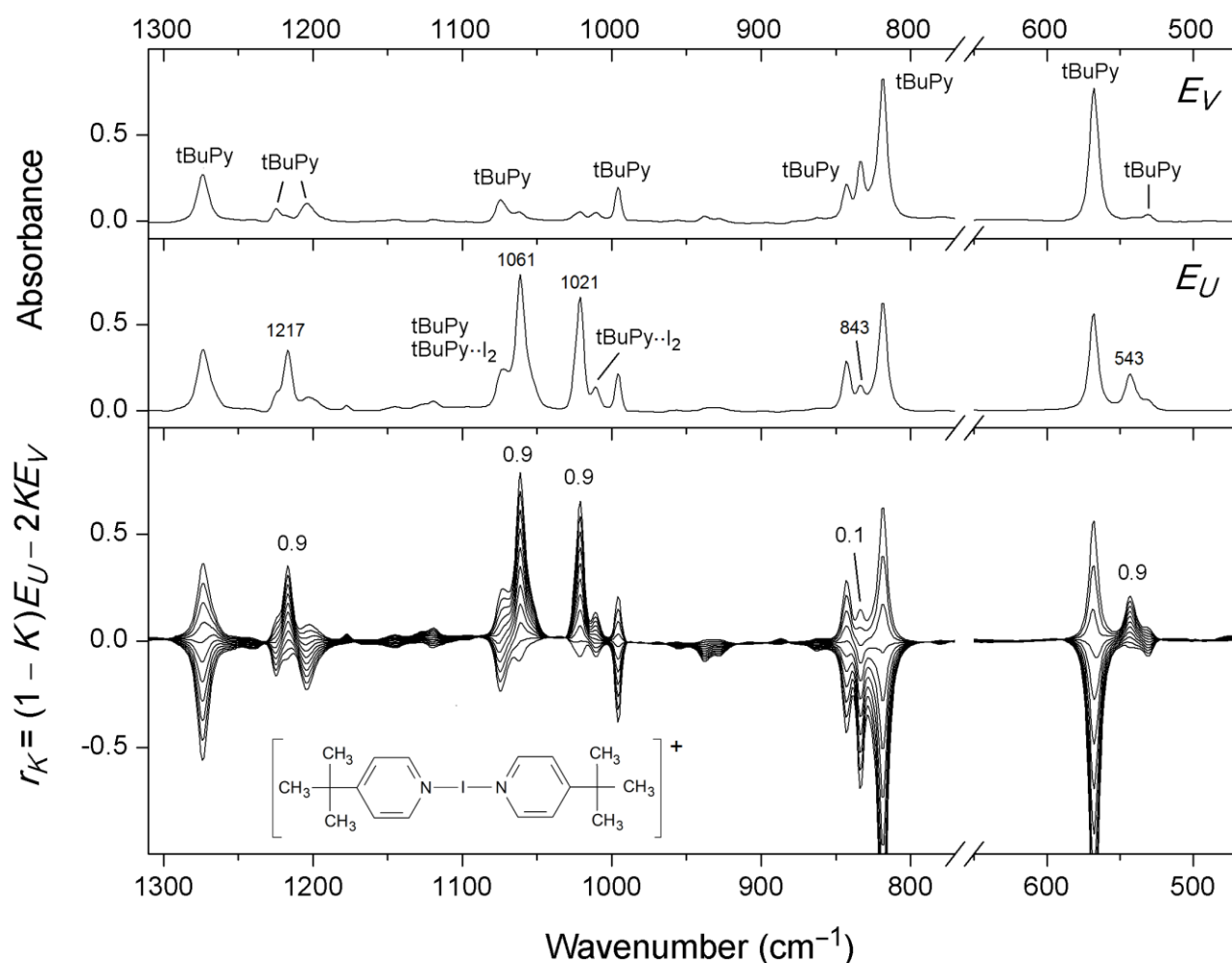


**Figure 3.** Isotropic absorption spectrum of the reaction products of 4-methylpyridine (MePy) and iodine in stretched polyethylene after one day at 22 °C. The main bands are assigned to the bis(4-methylpyridine)iodine(I) cation,  $(\text{MePy})_2\text{I}^+$ . Contributions due to MePy have been removed by subtraction.

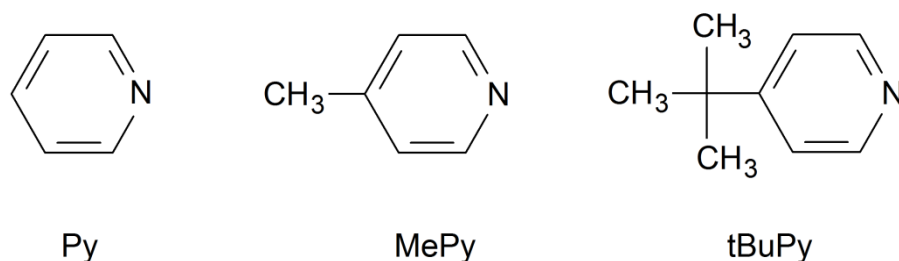




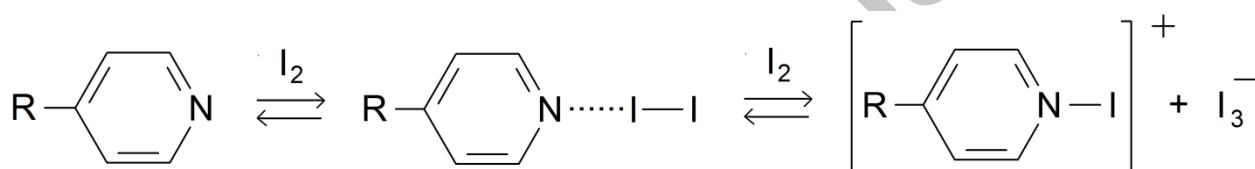
**Figure 4.** Isotropic absorption spectrum of the reaction products of 4-methylpyridine (MePy) and iodine in stretched polyethylene after one day at 50 °C. The main bands are assigned to the 4-methylpyridinium cation, MePyH<sup>+</sup>.



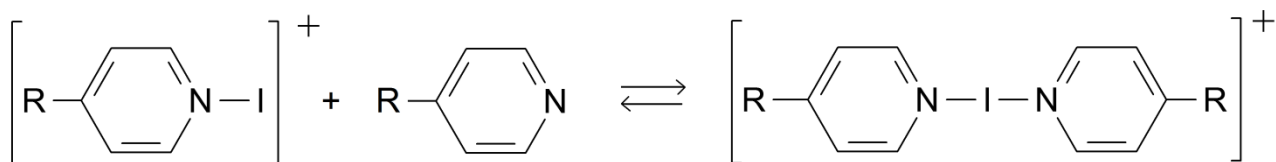
**Figure 5.** Top: Linear dichroic (LD) absorption curves  $E_U(\tilde{\nu})$  and  $E_V(\tilde{\nu})$  for the reaction products of 4-*tert*-butylpyridine (tBuPy) and iodine in stretched polyethylene after one day at 22 °C. Wavenumbers indicate prominent peaks assigned to the bis(4-*tert*-butylpyridine)iodine(I) cation, (tBuPy)<sub>2</sub>I<sup>+</sup>. Bottom: Family of reduced absorption curves  $r_K(\tilde{\nu}) = (1 - K) \cdot E_U(\tilde{\nu}) - 2K \cdot E_V(\tilde{\nu})$  for  $K$  ranging from 0 to 1 (see text). Resulting  $K$  values for prominent peaks assigned to (tBuPy)<sub>2</sub>I<sup>+</sup> are indicated.



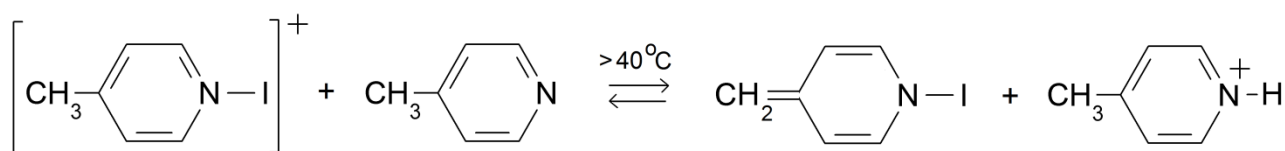
**Scheme 1.** Pyridine (Py), 4-methylpyridine (MePy), and 4-*tert*-butylpyridine (tBuPy).



**Scheme 2.**



**Scheme 3.**



**Scheme 4.** Possible proton transfer from 4-methyl-*N*-iodopyridinium (MePyI<sup>+</sup>) to 4-methylpyridine (MePy) to yield 4-methylidene-*N*-iodopyridine and 4-methylpyridinium (MePyH<sup>+</sup>).

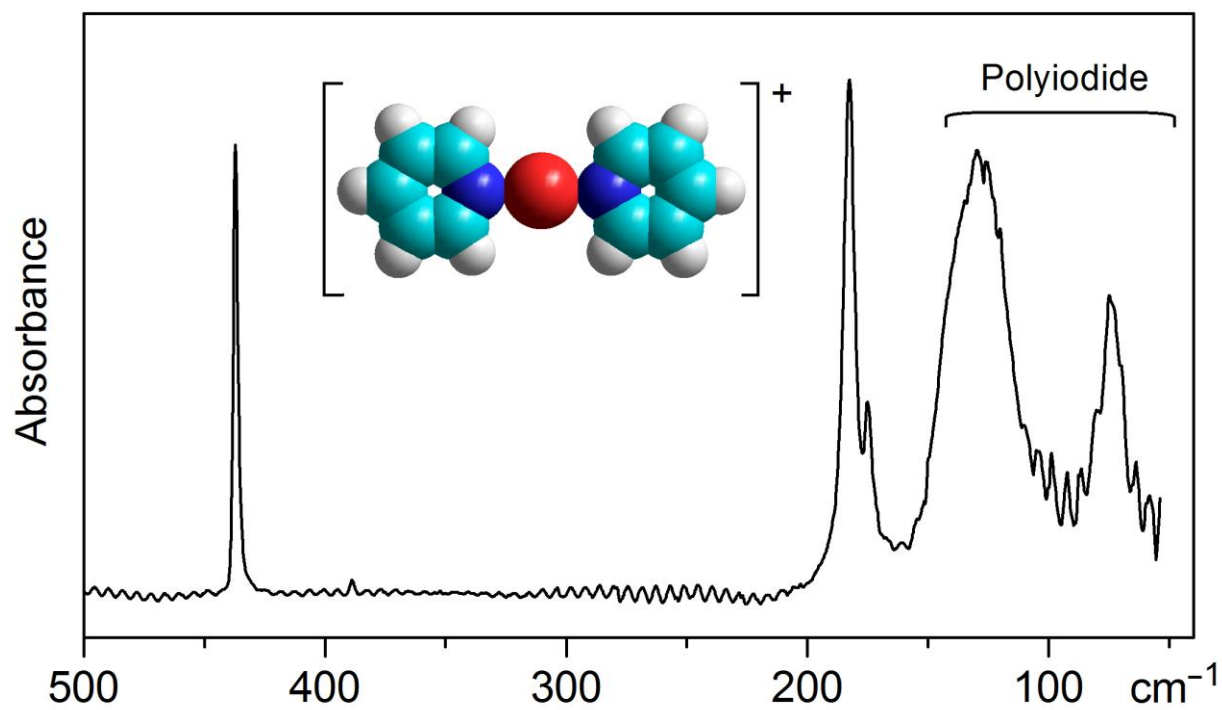
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## Graphical abstract



**Highlights:**

- Spontaneous formation of polyiodide salts in low-density polyethylene
- Vibrational fundamentals of the bis(pyridine)iodine(I) cation
- Bis(4-methylpyridine)iodine(I) and bis(*t*-butylpyridine)iodine(I) cations
- Formation of the 4-methylpyridinium cation at elevated temperature
- Possible formation of micro-crystalline polyiodide aggregates in polyethylene