

# H<sup>+</sup> Scattering in *n*-Butanol

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In this paper we show predictions for the low energy cross-sections and transport properties for the H<sup>+</sup> in *n*-butanol gas. These data are needed for modelling in numerous technologically important applications. Appropriate gas phase enthalpies of formation for the products were used to calculate scattering cross-section as a function of kinetic energy. Calculated cross-sections can be used to obtain transport parameters as a function of  $E/N$  ( $E$  — electric field,  $N$  — gas density) for H<sup>+</sup> in *n*-butanol gas.

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## 1. Introduction

*n*-Butanol (C<sub>4</sub>H<sub>9</sub>OH) also known as 1-butanol or *n*-butanol has a 4 carbon straight-chain structure, with the –OH at the terminal carbon. It is an important chemical feedstock used to produce solvents (butyl acetate, butyl glycol ethers) [1, 2], polymers (butyl acrylate, butyl methacrylate) [3] and plastics. But the recent interest in *n*-butanol is mostly due to its application as a biofuel for use in engines, as an alternative to conventional gasoline and diesel fuels [4–7]. Biofuels are attracting great interest as transportation fuels because they are renewable, can be locally produced, less polluting, more biodegradable, and reduce net greenhouse gas emissions [8]. *n*-Butanol, like ethanol, can blend with gasoline very well and could be a future option for blending with diesel. Butanol consists more oxygen content compared with biodiesel, leading to further reduction of the soot. *n*-Butanol occurs naturally as a minor product of the fermentation of sugars and other carbohydrates and is present in many foods and beverages as well as in a wide range of consumer products. Although most volatile organic compounds can be detected by fast methods such as ion mobility spectroscopy, precise determination is possible only if reaction of specific ions with targeted compound is well known.

*n*-Butanol is produced by alcoholic fermentation of the biomass feedstock [9–12] which include sugar beet, sugar cane, corn, wheat, and other various plant crops containing cellulose that could not be used for food and would otherwise go waste. Recently, the use of generically enhanced bacteria has also increased the fermentation process productivity.

The goal of this work is to calculate transport parameters of fragment ions of *n*-butanol. We employ Denpoh–Nambu’s theory (DNT) [13] to calculate transport cross-section sets for H<sup>+</sup> ions scattering on *n*-butanol appropriate for low energies of H<sup>+</sup> ions. By using Monte Carlo

technique of Ristivojević and Petrović [14] we calculated transport parameters as a function of  $E/N$ .

## 2. Cross-section sets

A calculation of the cross-sections would include the determination of the ion-neutral interaction potential energy surface, followed by quantum-mechanical calculations of the ion-neutral scattering processes [15]. All these tasks are tractable only if a certain level of approximation is introduced. There is another approach where it is possible to exploit some statistical theory [16] where the specific reaction rate for a unimolecular reaction may be used to obtain cross-section for each particular process [13, 17].

The scattering cross-sections of H<sup>+</sup> on *n*-butanol are calculated by using the DNT [13] separating elastic from reactive collisions. The induced dipole polarizability of  $8.9 \times 10^{-24}$  cm<sup>3</sup> [18] is used for the *n*-butanol target. In resemblance with our recent work [19] DNT has been used for separation of elastic from reactive endothermic collisions by accounting for the thermodynamical threshold energy and branching ratio according to the Rice–Rampersperger–Kassel (RRK) theory [20]. In the context of the RRK theory the internal energy is distributed among an empirical number of equivalent effective modes of the complex selected from the total number of atoms in the complex. Appropriate gas phase enthalpies of formation for the products [21] (Table I) were used to calculate thermodynamic thresholds. The cross-section for the exothermic reaction (EXO) forming a molecular ion H<sup>+</sup> in *n*-butanol is commonly represented by ion capture cross-section

$$\sigma_{exo} = \beta \sigma_L, \quad (1)$$

where  $\sigma_L$  is the orbiting cross-section [15] and  $\beta$  is the probability of a specific exothermic reaction.

In this calculation in the absence of resonant exothermic reactions we assumed that the probability of exothermic reactions is zero ( $\beta = 0$ ). In the low energy limit the cross-sections are similar due to dominant polarization of the target. At higher energies reactive collisions including the non-conservative collisions become efficient for various possible processes.

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It is well known that swarm method [22, 23] can be used to modify the cross-section for elastic momentum transfer if transport parameters are known. Thus elastic momentum transfer cross-section can be obtained if some initial, approximate, cross-section is available. For *n*-butanol transport parameters are not available [17]. We have separated the endothermic and exothermic processes by using the enthalpies from Ref. [21].

In this paper there are 20 exothermic processes. Exothermic process with lowest excess energy ( $H^+ + n$ -butanol  $\rightarrow C_3H_3OH^+ + C_3H_4 + H$ ) has 0.118 eV excess energy while lowest endothermic threshold ( $H^+ + n$ -butanol  $\rightarrow C_2H_4O^+ + C_2H_2 + 2H_2 + H$ ) is 0.061 eV. Therefore we have assumed in this work that exothermic processes are non-resonant, and neglected their effect on transport properties. With assumed product ions (Table I) we have selected 46 endothermic processes with thermodynamic thresholds up to about 11 eV. Elastic momentum transfer (MT) cross-section representing elastic collisions with isotropic scattering together with collisions where activated complex is back to reactants, and the cross-sections for collisions where  $H^+$  keeps on and where  $H^+$  is lost [13] are presented in Fig. 1.

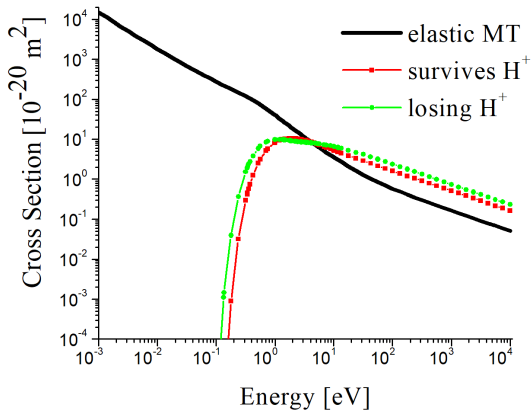


Fig. 1. Cross-sections for  $H^+$  ions in *n*-butanol.

### 3. Transport parameters

A precise treatment to obtain transport parameters ions of higher accuracy as a function of  $E/N$  would be to follow the solutions of generalization of the Boltzmann equation [24]. The Monte Carlo simulation methods are generally built around the same initial principles as related kinetic equations. In this work we apply the Monte Carlo simulation created for swarm particles [25, 26].

Transport properties of species in gas plasmas are of great importance in understanding the nature of molecular and ionic interactions in gas mixtures [27, 28]. These properties include the mean energy, drift velocity, diffusion coefficients, ionization and chemical reaction coefficients, chemical reaction coefficients for ions and rarely excitation coefficients, and they are very useful in chemical industries for the design of many types of transport

Heats of formation  $\Delta_f H^0$  at 298 K (kJ/mol) TABLE I

Species	$\Delta H_f^+$	$\Delta H_f^0$
H <sub>2</sub>	1488.3	0
CO	1241.59	-393.51
CO <sub>2</sub>	935.4	-393.51
CH <sub>2</sub> O	940.5	-108.7
H <sub>2</sub> O	975.0	-241.83
CH <sub>4</sub>	1132	-74.5
C <sub>2</sub> H <sub>4</sub>	1066	52.2
C <sub>2</sub> H <sub>6</sub>	1028	-84.0
C <sub>3</sub> H <sub>6</sub>	959	20.2
C <sub>3</sub> H <sub>8</sub>	227.5	951.5
C <sub>4</sub> H <sub>8</sub>	924	-0.4
C <sub>4</sub> H <sub>10</sub>	889	-126.5
CH <sub>4</sub> O	845.3	-201.6
C <sub>2</sub> H <sub>6</sub> O	775.4	-234.8
C <sub>3</sub> H <sub>8</sub> O	731	-254.8
C <sub>2</sub> H <sub>2</sub>	1327.9	228.0
C <sub>3</sub> H <sub>4</sub>	1186.2	186.6
C <sub>4</sub> H <sub>6</sub>	1033	162.3
C <sub>2</sub> H <sub>4</sub> O	821.1	-165.8
C <sub>3</sub> H <sub>6</sub> O	772.9	-187.4
C <sub>4</sub> H <sub>8</sub> O	742	-207.5

and process equipment. Swarm parameters, which are functions of reduced electric field  $E/N$  ( $E$  — electric field,  $N$  — gas density) in DC electric fields are usually applied to plasma modeling and simulations.

In this paper we have used a Monte Carlo code that properly takes into account the thermal collisions [14, 17]. The code has passed all the tests and the benchmarks that were covered in our earlier studies [17, 29]. Calculations are performed for the gas pressure 1 Torr and gas temperature of 300 K.

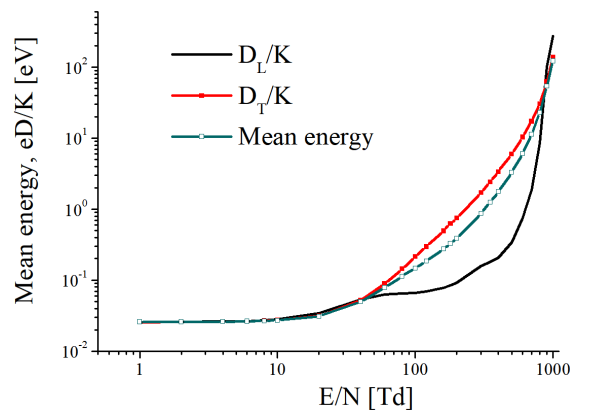


Fig. 2. Mean and characteristic energy as a function  $E/N$  for  $H^+$  ions in *n*-butanol.

In Fig. 2 we show characteristic energies (diffusion coefficient normalized by mobility  $eD/\mu$  in units eV) longitudinal (L) and transverse (T). We also show mean energy, which cannot be directly measured in experiments

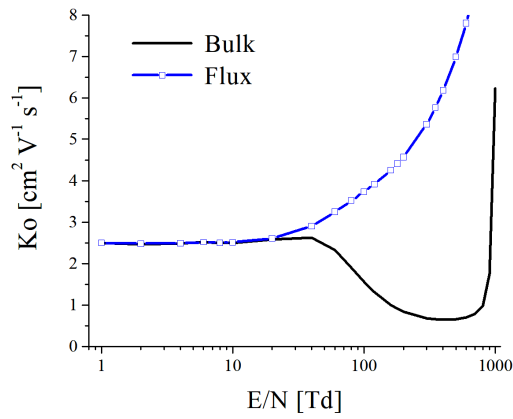


Fig. 3. Reduced mobility as a function  $E/N$  for  $H^+$  ions in  $n$ -butanol.

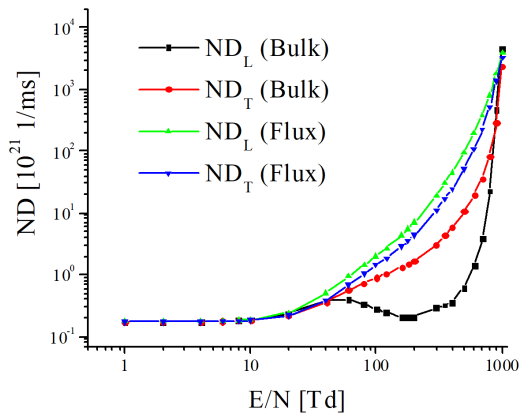


Fig. 4. Longitudinal and transversal diffusion coefficients as a function  $E/N$  for  $H^+$  ions in  $n$ -butanol.

but map of mean energy versus  $E/N$  may be used directly to provide the data in fluid models especially when local field approximation fails.

In Fig. 3 we show the results of Monte Carlo simulation for reduced mobility as a function of  $E/N$ . The mobility  $K$  of an ion is a quantity defined as the velocity attained by an ion moving through a gas under the unit electric field. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{\nu_d}{N_0 E} N, \quad (2)$$

where  $\nu_d$  is the drift velocity of the ion,  $N$  is the gas density at elevated temperature  $T$ ,  $N_0 = 2.6910^{25} \text{ m}^{-3}$  and  $E$  is the electric field. Due to reactive collisions bulk and flux values of reduced mobility are separated.

Longitudinal and transversal diffusion coefficients for  $H^+$  in  $n$ -butanol as a function of  $E/N$  are shown in Fig. 4. The peak is visible only in the behavior of longitudinal diffusion coefficients. Because of great capture of ions, we have a diminishing of NDL bulk values. However, there are no published experimental data for the longitudinal and transverse diffusion coefficients of  $H^+$  in  $n$ -butanol so far.

## 4. Conclusion

In this paper we show transport properties for the  $H^+$  in  $n$ -butanol which do not exist in the literature. The cross-section set has been determined by extending the Denpoh–Nanbu method.

The Monte Carlo technique was applied to carry out calculations of the mean energy, characteristic energy, reduced mobility and diffusion coefficients as a function of reduced DC electric field. The results are believed to be a good base for modeling, which could be further improved when measured values of transport coefficients become available and then we could perform this analysis again.

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