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Cross-sections for electron-scattering from 2-methyl-1-buten-3-yne, C_5H_6, molecules

Czesław Szmytkowski*, Sylwia Stefanowska, Elżbieta Ptasińska-Denga, Paweł Możejko**

Department of Atomic, Molecular, and Optical Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, ul G. Narutowicza 11/12, 80-233 Gdańsk, Poland

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ABSTRACT

Cross-sections for electron collisions with the 2-methyl-1-buten-3-yne [$H_2C{=}C(CH_3)C{\equiv}CH$] molecule were measured and calculated. Absolute *grand*-total electron-scattering cross-section (TCS) was taken at impact energies from 0.6 to 300 eV in the linear electron-transmission experiment. The TCS energy dependence for the electron–C_5H_6 collision has two prominent enhancements separated with a deep minimum located near 1.8 eV. In addition, in the low-energy TCS function two noteworthy features occur: (i) near 1 eV, a change in a slope on rapidly declining side of the TCS curve; (ii) between 2 and 5 eV, a distinct hump superimposed on the opposite, rising part of the curve. To search for the origin of these features in the TCS curve for C_5H_6, the comparison was made with results of the electron-scattering studies for selected hydrocarbon molecules. These features were attributed to the formation of short-living negative ions (resonant states). Elastic (ECS) and ionization (ICS) cross-sections for C_5H_6 and C_4H_2 (1,3-butadiyne) were computed up to 3 keV by means of the additivity rule (AR) approximation and the binary-encounter-Bethe (BEB) approach, respectively. For the C_5H_6 molecule, the sum ECS + ICS is in good agreement with the experimental TCS for energies above about 40 eV.

1. Introduction

Electron scattering on basic components of matter is a prominent tool for the investigation of fundamental processes in various media of scientific and technological importance [1–7]. Quantities describing the electron interactions with atoms and molecules are essential for modeling and controlling reactions in which electrons are involved [8]. In particular, comprehensive sets of measurables concerning collisions of electrons with hydrocarbons are of much interest due to the manifold prevalence and application of these compounds. Moreover, the diversity of hydrocarbon structures enables to study how the arrangement of components in target molecule influences the scattering pattern. However, for a number of hydrocarbons of scientific and practical importance the electron-scattering data are very scarce or are not available as yet (cf. Ref. [9]). The example of molecule for which the study on the electron scattering are not available in the literature is the 2-methyl-1-buten-3-yne [$H_2C{=}C(CH_3)C{\equiv}CH$] molecule, the simple compound containing the double and triple carbon-carbon bonds separated by one single C—C bond (cf. Fig. 2).

The 2-methyl-1-buten-3-yne molecules arose as the reaction product in the experiments in which gas mixtures representative of Titan's atmosphere were irradiated with UV light [10] or subjected to electrical discharges [11]. One can expect that electron-induced processes in planetary atmosphere of Titan would be of interest due to free electrons coming to the moon from Saturn's magnetosphere, as well as those involved in discharge phenomena. In this context, electron-scattering data would be useful in the interpretation of results obtained by the planetary probes and for modeling the evolution of planetary atmospheres, in particular those reactions which may lead to the formation of more complex organic compounds.

The aim of this work is to provide reliable cross-sections for the electron scattering from the 2-methyl-1-buten-3-yne molecule. Absolute *grand*-total cross-sections (TCS) were measured at impact energies ranging from 0.6 to 300 eV using the linear electron-transmission method. To discuss the observed TCS features, the current TCS results for the 2-methyl-1-buten-

* Principal corresponding author.
** Corresponding author.
E-mail addresses: czsz@mif.pg.gda.pl (C. Szmytkowski), sylstefa1@student.pg.gda.pl (S. Stefanowska), elzdenga@pg.edu.pl (E. Ptasińska-Denga), paw@pg.edu.pl (P. Możejko).

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3-yne [$H_2C{=}C(CH_3)C{\equiv}CH$] molecule were compared to previous experimental data for conjugated alkenes (2-methyl-1,3-butadiene [$H_2C{=}C(CH_3)HC{\equiv}CH_2$], and 1,3-butadiene [$H_2C{=}CHHC{=}CH_2$]) and to results for conjugated alkyne, 1,3-butadiyne [$HC{\equiv}C{-}C{\equiv}CH$]. To extend the electron–C_5H_6 scattering data beyond the experimental energy range, we also computed the integral elastic (ECS) and ionization (ICS) cross-sections up to 3 keV using the additivity rule (AR) approximation and the binary-encounter-Bethe (BEB) approach, respectively. The sum of ECS and ICS was compared to our experimental TCS data. Similar calculations were carried out for 1,3-butadiyne.

2. Measurements

Measurements of the absolute TCSs for the electron scattering from 2-methyl-1-buten-3-yne were performed using the linear electron-transmission method [12], over incident energy range from 0.6 to 300 eV. The experimental setup and measurement procedure used in this work were essentially those described in detail elsewhere [13], so only a brief outline is given here.

An energy dispersing 127° electrostatic deflector and an assembly of electrostatic lenses are used to form an electron beam of 80 meV energy resolution (FWHM) and typical intensity of 0.1–10 pA, which is allowed to pass along a static molecular target placed in the reaction cell. The electrons which emerged from the cell through the exit orifice enter a retarding field analyzer, which discriminates those scattered inelastically in the forward direction with a kinetic-energy difference of no more than 0.1 eV in the case of low impact energies and about 0.5 eV at intermediate energies. The transmitted electrons are finally collected in the Faraday trap detector. The acceptance angle of the used electron detector system, defined by the lens apertures, is near 0.8 msr. The energy of the incident electron beam is established with respect to the resonant oscillatory structure visible around 2.3 eV (see, e.g., [14,15]) when the N_2 is admixtured to the target under study. Electron optics of the spectrometer is housed in a vacuum chamber evacuated to a base pressure of about 40 μPa. The ambient magnetic field along the whole electron pathway in the spectrometer is reduced below 100 nT using the system of Helmholtz coils. No other magnetic fields are applied in the electron optics region.

The total cross-section, Q, at given electron impact energy, E, was derived based on measurements of the projectile electron-beam intensity attenuation while transmitted through the scattering medium according to the Bouguer–de Beer–Lambert (BBL) relation:

$$I_n(E) = I_0(E)\exp[-nLQ(E)], \tag{1}$$

where $I_n(E)$ is the measured intensity of the electron beam after traversing a length L of target medium whose the number density is n, and $I_0(E)$ is the intensity of the beam taken in the absence of the target molecules in the reaction cell. Following the Nelson and Colgate [16] calculations for the geometry and reaction volume of the present experiment, the length L is equal (within 0.5% accuracy) to the geometrical distance between entrance and exit orifices of the reaction cell (L = 30.5 mm). The number density, n, is evaluated from the ideal gas formula corrected for the thermal transpiration effect [17]

$$n = \frac{p_t}{k\sqrt{T_t T_m}}. \tag{2}$$

Here, p_t means the pressure of the vapor-target in the cell as measured by a capacitance manometer and k denotes the Boltzmann constant, T_t is the temperature of the target cell determined using a thermocouple, T_m = 322 K > T_t is the temperature at which the manometer head is held.

The sample (99%) of 2-methyl-1-buten-3-yne, from Sigma–Aldrich, was distilled by freeze–pump–thaw repetitive cycles before use to remove volatile impurities. The target vapor was admitted into the spectrometer via a variable leak valve, alternately into the reaction cell and the outer vacuum volume, thus the pressure in the region of the electron optics was maintained constant (below 0.6 mPa) whether or not the target was present in the cell; that ensured a stable primary electron-beam intensity during both phases of the intensity measurements. The TCS measurements have been carried out at target-vapor pressures between 70 and 200 mPa. Under these conditions no systematic variation of the measured TCSs with the target pressure was observed; thus one can assume that multiple scattering events were not significant.

The quantities in the attenuation BBL formula are taken directly in the course of the experiment and therefore the TCS values reported in this work are given in absolute units, without any normalization procedure. The final TCS at given impact energy was derived as the weighted average of TCS values obtained in different runs.

3. Theory

To extend present results beyond energies accessible in our experiment and to discuss contribution from elastic and ionization channels to the measured total cross-section, we have performed calculations of elastic and ionization cross-sections. Cross-section for the elastic electron scattering has been obtained with the additivity rule (AR) which is based on the independent atom method IAM) [18–20]. Total cross-section for single electron-impact ionization of the studied target has been calculated using binary-encounter-Bethe (BEB) model. The theoretical approach and computational procedures applied in the present work are essentially the same as those used in our previous calculations [21,22]. Thus, only a short description of the methods and procedures is given here.

In elastic cross-section calculations within the AR approximation, the question of electron-molecule scattering is reduced to the electron-atom collision problem if the following assumptions are fulfilled [19]: (i) each atom of the molecule scatters independently; (ii) any redistribution of atomic electrons due to the molecular binding is unimportant so that each atom scatters as if it were free; (iii) multiple scattering within the molecule is negligible.

The elastic cross-section for electron scattering on the molecule in this approximation is given by

$$\sigma(E) = \sum_{i=1}^{N} \sigma_i(E), \tag{3}$$

where $\sigma_i(E)$ is the integral cross-section of the ith atom of the molecule, $E = k^2/2$ is the energy of the incident electron and k is the wave number of the incident electron (in this section the atomic units are used).

To obtain atomic scattering amplitudes and the elastic electron-atom cross-sections we employed partial wave analysis and solved numerically the radial Schrödinger equation

$$\left[\frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{l(l+1)}{r^2} + k^2 - 2\left(V_{\mathrm{stat}}(r) + V_{\mathrm{polar}}(r)\right)\right] u_l(r) = 0 \tag{4}$$

under the boundary conditions

$$u_l(0) = 0, \quad u_l(r) \overset{r\to\infty}{\longrightarrow} A_l \hat{j}_l(kr) - B_l \hat{n}_l(kr). \tag{5}$$

Interaction of the incident electron with atom is described within static-polarization approximation only, by the static potential,