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How to cite:
Thakar, Yogesh; Bhavsar, Rakesh; Swadia, Mohit; Vinodkumar, Minaxi; Mason, Nigel and Limbachiya, Chetan (2019). Electron interactions with astro chemical compounds. Planetary and Space Science, 168 pp. 95–103.

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Version: Accepted Manuscript

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ELECTRON INTERACTIONS WITH ASTRO CHEMICAL COMPOUNDS

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ABSTRACT

In present work electron induced processes with important astro-compounds found in the tholins of Titan are investigated. We report calculated total elastic cross sections Q_{el}, total inelastic cross sections Q_{inel}, total ionization cross sections Q_{ion}, total excitation cross sections \( \Sigma Q_{exc} \) and total cross sections Q_T for hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH_2CHCN), methanimine (CH_2NH) and ethanimine (CH_3CHNH) on electron impact for energies from ionization threshold to 5keV. We have employed the Spherical Complex Optical Potential (SCOP) formalism to investigate elastic as well as inelastic processes and used Complex Scattering Potential – ionization contribution (CSP-ic) method to derive ionization cross sections. In absence of any theoretical or experimental data of ionization cross sections except for HCN and HCCCN, we have computed Q_{ion} using the Binary- Encounter- Bethe (BEB) method for all these molecules and have found reasonable agreement. This is the maiden attempt to report various total cross sections for all these astro-molecules except HCN and HCCCN.

Keywords: Astrochemical compounds; Titan atmosphere; Electron scattering
INTRODUCTION

The development of modern space based telescopes (e.g Hubble) and large ground based arrays like Atacama Large Millimeter/submillimeter Array (ALMA) has revealed a rich chemical inventory in the interstellar medium, star and planet forming regions as well as various cometary and planetary environments [1]. Such discoveries are fundamental to our exploration of how prebiotic chemistry evolved to develop life on Earth and underpin our investigations of whether life has developed elsewhere. One particularly well studied environment that is believed to provide a mimic for a prebiotic Earth is Titan, the largest satellite of Saturn. Organic chemical reactions in Titan’s atmosphere, induced by solar radiation and charged particles including electrons coming from Saturn’s magnetosphere [2, 3] provide a test-bed for prebiotic chemistry.

The dense atmosphere of Titan primarily consists of nitrogen and methane [4]. Cosmic rays, UV radiation coming from the Sun and Saturn’s magnetosphere induce electron bombardment that causes dissociation of N\textsubscript{2} and CH\textsubscript{4} leading to complex organic chemistry at higher altitudes on Titan and results in generation of solid aerosols responsible for orange haze surrounding the satellite [5]. Several experiments have been developed to reproduce and study such complex atmospheres in a laboratory [6, 7]. Carrasco and coworkers have developed a plasma device PAMPRE (French acronym for Production d’Aerosols en Microgravité par Plasma REactifs – Aerosols Production in Microgravity by Reactive Plasma) that has provided significant clues in the understanding of the polymeric chemical structure of the aerosols [8]. The goal of the PAMPRE experiment is to simulate Titan’s atmospheric chemistry including the chemical reactivity causing the formation of aerosols, by producing laboratory analogues of these aerosols [6, 9]. A spectrometer aboard the Cassini spacecraft showed formation of tholins in Titan’s atmosphere at altitudes greater than 1000 km [5]. The instruments on-board the recently completed Cassini-Huygens mission (NASA/ESA) have exposed new features of Titan’s
atmospheric chemistry finding many important molecules, and revealing negative and positive ions in its upper atmosphere [10-14]. Numerical methods are employed to investigate the chemical trail and mechanisms to describe these observations [8, 15-19]. However, such studies (laboratory, observational and modelling) are limited by our poor knowledge of the electron interactions with many of the tholin related compounds. Moreover, electron interactions with molecules of astrochemical interest lead to the chemistry of formation of other compounds and even amino acids which are considered as precursors for life.

In this work we investigate electron interactions with several tholin related compounds and compute the probabilities of occurrence of various electron-driven processes quantitatively through several total cross sections. We have studied hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH₂CHCN), methanimine (CH₂NH) and ethanimine (CH₃CHNH) all found in the dense tholins of Titan [6, 7]. Methanimine and vinyl cyanide have also been detected in sagattarius-B2 [20, 21] which is a dense interstellar cloud towards the center of the Milky Way. Methanimine is an important molecule in astrobiology since it is an amino acid precursor [22] and when it reacts with hydrogen cyanide, it can form simplest amino acid, glycine. It is protonated imine and is detected in Titan’s Ion Neutral Mass Spectrometer (INMS) measurements reinforcing the suspected role of chemical species on aerosol production [7]. Vinyl cyanide is highly flammable and toxic. It is commonly observed in hot cores of interstellar clouds which are sites of formation of massive stars and it has also been detected at lower abundance in cold interstellar clouds [23].

Ethanimine is an organo-nitrogen compound classified as an imine. It is not well known terrestrially but has been detected in abundance towards Sagittarius B2 (Sgr B2) [24]. It is mainly found in hot cores of ISM clouds e.g, in Sgr B2[25]. Cyanoacetylene is a linear polar
molecule found in the upper atmosphere of Titan [6, 7] as well as in the coma of the comet Hale-Bopp [26]. Hydrogen cyanide is the feed gas for the CN laser system [27-29] and has been detected in comets and in the interstellar region [30, 31]. Its dipole moment (2.98 D) is larger than the critical value (1.625 D) at which polar molecule may support bound negative ion states and it is therefore important from fundamental theoretical point of view and hence it is a case study for anion chemistry [32] along with being astro-chemically important [33]. In figure 1 we show schematic diagrams of these molecules.

![Schematic Diagram of Molecules](https://commons.wikimedia.org)

(a) Hydrogen cyanide (HCN)  
(b) Cyanoacetylene (HCCCN)  
(c) Vinyl cyanide (CH$_2$CHCN)  
(d) Methanimine (CH$_2$NH)  
(e) Ethanimine (CH$_3$CHNH)

**Figure 1 schematic diagram of the molecules**

Although, electron interactions with these compounds are important, a literature survey reveals that no electron impact data for these molecules except HCN and HCCCN is reported in the current energy range (ionization threshold to 5000 eV). We present survey of previous study on
electron-driven processes concerning present work along with the range of impact energy in table 1.

In fact, the lack of experimental investigations for these molecules may be ascribed to their toxicity and unavailability in gaseous phase. This motivated us to perform a detailed study of electron interactions with hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH₂CHCN), methanimine (CH₂NH) and ethanimine (CH₃CHNH) at energies starting from circa ionization threshold (~10 eV) to 5000 eV [34].

**Table 1: Previous study on electron impact cross sections**

<table>
<thead>
<tr>
<th>Target</th>
<th>Quantity</th>
<th>Impact energy range (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen cyanide (HCN)</td>
<td>Qₑ, Qinel, Qₜ</td>
<td>Threshold to 5000 eV</td>
<td>Jain and Baluja [35]</td>
</tr>
<tr>
<td></td>
<td>Qₜ</td>
<td>Threshold to 10000 eV</td>
<td>Sanz et al. [36]</td>
</tr>
<tr>
<td></td>
<td>Q₁₀₀</td>
<td>Threshold to 5000 eV</td>
<td>Pandya et al. [33]</td>
</tr>
<tr>
<td></td>
<td>Qₜ</td>
<td>100 eV to 5000 eV</td>
<td>De Hang et al. [37]</td>
</tr>
<tr>
<td></td>
<td>Qₜ</td>
<td>3 eV, 11.6 eV, 21.6 eV and 50 eV</td>
<td>Srivastava et al. [32]</td>
</tr>
<tr>
<td>Cyanoacetylene (HCCCN)</td>
<td>Q₁₀₀</td>
<td>Threshold to 200 eV</td>
<td>Gilmore and Field [38]</td>
</tr>
<tr>
<td></td>
<td>Q₁₀₀, Qₑ</td>
<td>Threshold to 5000 eV</td>
<td>Kaur et al. [39]</td>
</tr>
<tr>
<td>Methanimine (CH₂NH)</td>
<td>Qₑ</td>
<td>0 to 10 eV</td>
<td>Wang et al. [40]</td>
</tr>
</tbody>
</table>

We have evaluated total cross sections, Qₜ, total elastic cross sections, Qₑ, total inelastic cross sections, Qinel, total ionization cross sections, Q₁₀₀ and summed total excitation cross sections, \( \sum Q_{exc} \) for electron interactions with these molecules.
THEORETICAL METHODOLOGY

The present calculations make use of two distinct methodologies, namely the Spherical Complex Optical Potential (SCOP) [41-43] and the Complex Scattering Potential-ionization contribution (CSP-ic) [44, 45], which are appropriate for intermediate to high impact energies (ionization threshold to 5000 eV) to investigate various molecular processes upon interactions with electrons. We present molecular properties which are employed for this computational work in table 2.

Table 2: Properties of target molecules [46]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Ionization Potential (eV)</th>
<th>Bond lengths</th>
<th>Polarizability (Å³)</th>
<th>Dipole-moment (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen cyanide</td>
<td>13.60</td>
<td>C–H(1.064), C≡N (1.156)</td>
<td>2.59</td>
<td>2.98</td>
</tr>
<tr>
<td>(HCN)</td>
<td></td>
<td>C≡N(1.160), C–C(1.376)</td>
<td>5.40</td>
<td>3.72</td>
</tr>
<tr>
<td>Cyanoacetylene</td>
<td>11.62</td>
<td>C≡N(1.160), C–C(1.376)</td>
<td>5.40</td>
<td>3.72</td>
</tr>
<tr>
<td>(HCCCN)</td>
<td></td>
<td>C≡C(1.206), C–H(1.062)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vinyl cyanide</td>
<td>10.91</td>
<td>C–C(1.426), C≡C (1.339)</td>
<td>8.05</td>
<td>3.87</td>
</tr>
<tr>
<td>(CH₂CHCN)</td>
<td></td>
<td>C–H(1.086), C≡N (1.164)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanimine</td>
<td>09.97</td>
<td>C=N(1.273), N=H (1.023)</td>
<td>2.47</td>
<td>2.00</td>
</tr>
<tr>
<td>(CH₂NH)</td>
<td></td>
<td>C–H(1.081)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanimine</td>
<td>09.50</td>
<td>C–H(1.087), N–H (1.004)</td>
<td>5.30</td>
<td>1.90</td>
</tr>
<tr>
<td>(CH₃CHNH)</td>
<td>[47]</td>
<td>C≡N(1.249), C–C (1.499)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Spherical complex optical potential (SCOP) formalism**

The SCOP method [41-43] exploits the potential scattering formalism to estimate the total probabilities for elastic as well as inelastic processes in terms of total cross sections such that,

\[ Q_T(E_i) = Q_{el}(E_i) + Q_{inel}(E_i) \]

(1)

where \( E_i \) is the incident energy of electrons.

Here \( Q_T(E_i) \) represents the sum of all the possible elastic as well as inelastic processes induced by the incident electrons under the spherical approximation.

The potential scattering involves solving of the time independent Schrödinger equation with the complex optical potential corresponding to the electron-molecule system defined as,

\[ V_{opt}(r, E_i) = V_R(r, E_i) + i V_I(r, E_i) \]

(2)

Here \( V_R(r, E_i) \) is real and \( V_I(r, E_i) \) is an imaginary part of the potential that describe elastic and inelastic interactions respectively. While the real part of the potential comprises of the static potential \( V_{sc}(r) \), exchange potential \( V_{ex}(r, E_i) \) and polarization potential \( V_{pol}(r, E_i) \), the imaginary part corresponds to the absorption potential \( V_{ab}(r, E_i) \). All these potentials are evaluated by means of spherically averaged molecular charge density \( \rho(r) \) computed using the Hartree-Fock wave functions [48].

To describe the electron exchange we used Hara ‘Free Electron Gas Exchange’ (HFEGE) model [49] given by,

\[ V_{ex} = -\frac{2}{\pi} k_p \left( \frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right) \]

(3)
Where,

\[ \eta = \frac{\sqrt{k^2 + k_F^2 + 2I}}{k_F} \]

Here \( k \) is the incident energy of the electrons, \( k_F \) is the Fermi wave vector and \( I \) is the ionization potential of the molecule under investigation.

While a correlation polarization potential model [50] is employed to describe the polarization effect, all inelastic effects are taken care of by a non-empirical quasi-free absorption potential model [51]

\[ V_{abs}(r, E_i) = -\rho(r) \sqrt{\frac{T_{loc}}{2}} \left( \frac{\eta \pi}{10 k_F^2 E_i} \right) \theta(p^2 - k_F^2 - 2\Delta)(A_1 + A_2 + A_3) \quad (4) \]

The \( T_{loc} \) is the local kinetic energy of the incident electrons; \( k_F \) is Fermi vector and \( \theta(X) \) is the Heaviside unit step-function. The dynamic functions \( A_1, A_2 \) and \( A_3 \) depend upon the ionization potential \( I \) and the energy parameter \( \Delta \) that decides a threshold below which, \( V_{abs}(r, E_i) = 0 \), which means ionization and excitation are energetically forbidden [52]. Magnitude of total inelastic cross section is determined through factor \( \Delta \) [51, 53]. We have modified the original model by considering \( \Delta \) as a slowly varying function of \( E_i \) around \( I \) allowing the electronic excitations to occur below the ionization threshold of the target [53, 54] such that,

\[ \Delta(E_i) = 0.8I + \beta(E_i - I) \quad (5) \]

For \( E_i = I \), we get minimum value of \( \Delta \). The second term corresponds to energy dependence of \( \Delta \) before it attains maximum value \( I \). This energy dependence is governed by parameter \( \beta \) which is determined by imposing the condition \( \Delta = I \) at \( E_i \geq E_p \). Here \( E_p \) is the energy at which we get maximum \( Q_{inel} \).
Complex Scattering Potential – ionization contribution (CSP-ic) technique

In order to estimate the ionization probabilities we use CSP-ic method [52, 55]. We define a dynamic ratio,

\[ R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)} \]  

Here \( 0 < R \lesssim 1 \). The ratio is evaluated using the following conditions,

\[ R(E_i) \begin{cases} = 0 \text{ for } E_i \leq I \\ = R_P \text{ at } E_i = E_p \\ \cong 1 \text{ for } E_i \gg E_p \end{cases} \]  

Where, \( R_P \) is the magnitude of \( R(E_i) \) at \( E_i = E_p \).

Turner et al. [56] described importance of ionization compared to excitation. They concluded from semi-empirical calculations for gaseous H₂O that if \( \sigma_{ion} \) and \( \sigma_{exc} \) are the cross sections of the ionization and excitation respectively then, above 100 eV [56].

\[ \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{exc}} \approx 0.75 \]  

Here, \( \sigma_{ion} \) and \( Q_{ion} \) are same but we preserve notations in equation (8) as per reference paper [56].

For many stable molecules like O₂, H₂O, CH₄, etc. experimental ionization cross section are accurately known [53, 57, 58] and it is found that maximum contribution of \( Q_{ion} \) to the total inelastic cross sections, \( Q_{inel} \) is 70-80\%. This tendency is because of the reducing values for \( \sum Q_{exc} \) compared to \( Q_{ion} \) at higher energies.

The above ratio is determined using the following analytical form [44, 53, 55].

\[ R(E_i) = 1 - C_1 \left( \frac{C_2}{U+a} + \frac{ln(U)}{U} \right) \]
With \( U = \frac{E_i}{T} \).

At higher energies, the ratio \( R(E_i) \) tends to unity since \( Q_{\text{ion}} \) forms major part of inelastic cross sections and the total excitation cross sections \( \sum Q_{\text{exc}} \) reduce. Moreover the discrete excitation cross sections, mainly due to dipole transitions, reduce as \( \frac{\ln(U)}{U} \) at higher energies. The dimension free parameters \( C_1, C_2 \) and \( a \) depend upon the properties of the target under study and they are evaluated using equation (9). We finally compute \( Q_{\text{ion}} \) vide equation (6).

We have also calculated \( Q_{\text{ion}} \) with the help of the Binary-Encounter-Bethe (BEB) method [59]. This well-established method includes the Mott cross sections with the high energy tendency of Bethe cross sections [59]. The BEB model features an analytic relation that uses the energy of incidence, the binding and kinetic energies of the molecule to give the ionisation cross sections with an uncertainty of 10-20\% in the non-relativistic description of BEB [59, 60]. Electron-impact ionization of an atom is given by an expression for the cross section of each molecular orbital as:

\[
\sigma_{\text{BEB}}(t) = \frac{s}{t+u+1} \left[ \frac{\ln(t)}{2} \left( 1 - \frac{1}{t^2} \right) + 1 - \frac{1}{t} \ln(t) \right] \quad (10)
\]

Here, \( t = \frac{T}{B}, u = \frac{U}{B}, s = \frac{4\pi a_0^2 N R^2}{b^2}, a_0 \) is the Bohr radius (0.529 Å), \( R \) is the Rydberg energy and \( T \) is the incident electron energy. \( N, B \) and \( U \) are the electron occupation number, the binding energy and average kinetic energy of the orbital respectively.

We have calculated \( Q_{\text{ion}} \) data for the present molecules using BEB formula [61] to offer a comparison with the results of the CSP-ic method [44, 62, 63] which employs various additivity rules. In the CSP-ic method we use group additivity rule [62] to develop molecular charge density from the atomic charge densities. At lower incident energies, the molecular target is treated as a multi-center body and different atomic groups with larger bond lengths can be
treated as separate scattering centers. We define several such groups at the charge density as well as potential level. This treatment is governed by various bond lengths and the atomic number of the constituent atoms. The charge densities of lighter atoms are superimposed on heavier atoms or center of mass depending upon the geometry of the molecule. At high energies the molecule is seen as a single entity.

**RESULTS AND DISCUSSION**

In this work we have done an exhaustive study of electron interaction with five important astrochemical molecules found in the tholins of Titan, hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH$_2$CHCN), methanimine (CH$_2$NH) and ethanimine (CH$_3$CHNH).

We present the results along with available comparisons in two categories - (A) **Inelastic cross sections**: In this segment we report graphical results of $Q_{inel}$, $Q_{ion}$ and $\sum Q_{exc}$. The $Q_{ion}$ are computed using both, the CSP-ic and the BEB method (B) **Elastic cross sections**: In this segment we report the present results on $Q_{el}$ and $Q_T$.

**(A) Inelastic cross sections**

Electron driven inelastic cross sections are quantitatively reported through $Q_{inel}$, $Q_{ion}$ and $\sum Q_{exc}$ in figures 2 to 6 for hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH$_2$CHCN), methanimine (CH$_2$NH) and ethanimine (CH$_3$CHNH) respectively along with previous data wherever available for energies from ~ionization potential to 5000 eV.

The upper most curves in each of these figures (figure 2 to 6) show present total inelastic cross sections, $Q_{inel}$ that encompasses all the spherical inelastic processes and represents an upper limit for inelastic scattering cross sections. The spherical inelastic processes include only electronic excitation and ionization. In this study we do not consider the non-spherical effects such as
rotations and vibrations of the molecule. Except for HCN, we have not found any data of total inelastic cross sections, $Q_{\text{inel}}$ for these molecules. We have also shown the total ionization cross section $Q_{\text{ion}}$ in these figures (figure 2 to 6). We have calculated $Q_{\text{ion}}$ using two methods, CSP-ic [63] and BEB [59]. All of these results are sensitive to the target geometry, charge density and the ionization potential. In the CSP-ic method we have used the target properties listed in table 1.

The total cross sections, $Q_{\text{inel}}$, $Q_{\text{ion}}$ and $\sum Q_{\text{exc}}$ for e-HCN are shown in figure 2 along with available comparison. As shown in figure 2, present $Q_{\text{inel}}$ data show excellent agreement with the theoretical data of Jain and Baluja [35] across the present energy range. The SCOP theory adopted by Jain and Baluja [35] employs different model potentials to define the electron–molecule interactions. Moreover, they have used a constant $\Delta=I$ for the absorption potential in equation (4), which does not allow the discrete excitation processes below the ionization potential. The present $Q_{\text{inel}}$ underestimates the results of Sanz et al. [36] significantly. This is due to the Screen Corrected Independent Atom Model (SC-IAM) adopted by Sanz et al. [36], which neglects the molecular bonding and the geometry of the target considered. Here, we have considered bond lengths and geometry of the targets for calculation of molecular charge density from the atomic charge densities [48] using geometrical models [63]. Additionally, Sanz et al. [36] have quoted an uncertainty of 10 -20% due to interpolation between 30 - 50 eV. Their data merges with the present $Q_{\text{inel}}$ above 200 eV since the inelastic cross sections fall as $\ln (E_i)/E_i$ at higher energies.

As shown in figure 2 for HCN, the BEB results of $Q_{\text{ion}}$ rise rapidly at threshold and are slightly higher compared to the values of $Q_{\text{ion}}$ calculated using CSP-ic method particularly at the peak. This behavior at the $Q_{\text{ion}}$ (peak) is mainly due to the lower Koopman ionisation potential [64] for
HCN. Below 30 eV, present CSP-ic results differ from the BEB results of Pandya et al [33].

While the two BEB results show excellent matching, the CSP-ic data of Pandya et al. [33] is shifted leftwards. Pandya et al [33] have studied HCN using different models to develop the molecular charge distribution.

![Diagram showing Q\text{inel}, Q\text{ion} and \Sigma Q\text{exc} for e-HCN scattering]

**Fig. 2** Q\text{inel}, Q\text{ion} and \Sigma Q\text{exc} for e-HCN scattering

- Solid line: Present Q\text{inel}; Dash line: Present Q\text{ion} (CSP-ic); Dash Dot line: Present Q\text{ion} (BEB)
- Short Dot line: Pandya et al Q\text{ion} [33]; Short Dash Dot line: Pandya et al Q\text{ion} (BEB) [33];
- Dash Dot Dot line: Jain and Baluja Q\text{inel} [35]; Short Dash line: Sanz et al. Q\text{inel} [36]; Dot line: Present \Sigma Q\text{exc}
**Fig. 3** \( Q_{\text{inel}} \) \( Q_{\text{ion}} \) and \( \sum Q_{\text{exc}} \) for e-HCCCN scattering

Solid line: Present \( Q_{\text{inel}} \); Dash line: Present \( Q_{\text{ion}} \) (CSP-ic); Dash Dot line: Present \( Q_{\text{ion}} \) (BEB); Dash Dot Dot : Gilmore \( Q_{\text{ion}} \) (BEB) [38]; Short Dash : Kaur et al. \( Q_{\text{ion}} \) (CSP-ic) [39]; Short Dot: Kaur et al. (BEB) [39]; Dot line: Present \( \sum Q_{\text{exc}} \)

**Fig. 4** \( Q_{\text{inel}} \) \( Q_{\text{ion}} \) and \( \sum Q_{\text{exc}} \) for e-CH\(_2\)CHCN scattering

Solid line: Present \( Q_{\text{inel}} \); Dash line: Present \( Q_{\text{ion}} \) (CSP-ic); Dash Dot line: Present \( Q_{\text{ion}} \) (BEB); Dot line: Present \( \sum Q_{\text{exc}} \)
Fig 5 $Q_{\text{inel}}$, $Q_{\text{ion}}$ and $\sum Q_{\text{exc}}$ for e-CH$_2$NH scattering

Solid line: Present $Q_{\text{inel}}$; Dash line: Present $Q_{\text{ion}}$ (CSP-ic); Dash Dot line: Present $Q_{\text{ion}}$ (BEB); Dot line: Present $\sum Q_{\text{exc}}$

In figure 3 we have displayed the results of HCCCN and have compared present results of $Q_{\text{ion}}$ with the previous BEB data of Gilmor and Field [38] and Kaur et al. [39] as well as CSP-ic data of Kaur et al [39]. The present data underestimate both the previous work [38, 39] but have similar nature of the cross section curve. Differences between the $Q_{\text{ion}}$ results obtained through CSP-ic and BEB formalisms are attributed to two aspects (1) In BEB method the ionization potential is computed using the Koopmans theorem [64] and it differs with most experimental ionization potential by about 1 eV. (2) The CSP-ic computation employs various group additivity rules (GAR) [62, 65] to model the charge density as well as the optical potential and $Q_{\text{ion}}$ are computed using the dynamic ratio $R(E_i)$ through the parameters $C_1$, $C_2$ and $a$ in equation (4). These differences in cross sections are expected since the BEB data are precise within about 10% accuracy with other measurements and theoretical results [44, 66].

In figure 4, we show present results of e- CH$_2$CHCN scattering for which no comparison is found in literature. The present $Q_{\text{ion}}$ as computed by both the methods show good matching owing to little difference between the ionization potentials used for CSP-ic and the BEB method. The $Q_{\text{inel}}$ as well as $\sum Q_{\text{exc}}$ rise steadily and attain peak at 64 eV and 50 eV respectively.

The cross sections for methanimine (CH$_2$NH) and ethanimine (CH$_3$CHNH) are shown in fig 5 and 6 respectively. For both these cases the $Q_{\text{ion}}$ (CSP-ic) attains higher peak value than the $Q_{\text{ion}}$
(BEB) because of the difference in the IP used for the CSP-ic and the Koopman IP used for the BEB computations. The discrete excitation cross sections $\sum Q_{\text{exc}}$ and the total inelastic cross sections $Q_{\text{inel}}$ are also shown. In table 3 we present the Koopman ionization potential [64] used for BEB calculations along with IP used for CSP-ic method [46, 47]. The influence of ionization potential (IP) on the $Q_{\text{ion}}$ is displayed through $Q_{\text{ion}}$ (peak) values found for the CSP-ic and BEB calculations in table 3. We also present the computed parameters used in equation (9) and $R_p$ for each molecule for the present study.

Table 3 Values of IP, $R_p$, $Q_{\text{ion}}$ (peak) and parameters C1, C2 and $a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>IP (eV)</th>
<th>Parameters</th>
<th>$Q_{\text{ion}}$ (peak) ($\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CSP-ic</td>
<td>BEB</td>
<td>C1</td>
</tr>
<tr>
<td>Hydrogen cyanide (HCN)</td>
<td>13.60</td>
<td>13.54</td>
<td>-0.879</td>
</tr>
<tr>
<td>Cyanoacetylene (HCCCN)</td>
<td>11.62</td>
<td>13.64</td>
<td>-0.800</td>
</tr>
<tr>
<td>Vinyl cyanide (CH$_2$CHCN)</td>
<td>10.91</td>
<td>11.28</td>
<td>-0.873</td>
</tr>
<tr>
<td>Methanimine (CH$_2$NH)</td>
<td>09.97</td>
<td>14.96</td>
<td>-0.858</td>
</tr>
<tr>
<td>Ethanimine (CH$_3$CHNH)</td>
<td>09.50</td>
<td>13.73</td>
<td>-0.905</td>
</tr>
</tbody>
</table>

As can be seen from table 3, the Koopman IP is somewhat larger than the experimental IP that we used [46, 47] for CSP-ic calculations except for HCN. Therefore the $Q_{\text{ion}}$ (peak) (BEB) for all
the molecules is lower than the $Q_{\text{ion}}$ (peak) (CSP-ic) except for HCN. In table 3, we have also quoted $R_p$, the value of $R(E_p)$, which is 0.7 as suggested by Turner et al [56]. The parameters involved in the theory and computation of $R_p$ renders semi-emperical nature to the theory.

In present calculations through CSP-ic method we identify the relative contribution of excitation processes compared with ionization in the form of the summed-total excitation cross-sections $\Sigma Q_{\text{exc}}$. The lower most curves in figure 2 to 6 show present $\Sigma Q_{\text{exc}}$. It is seen that, for all of these targets, the $\Sigma Q_{\text{exc}}$ rises quickly and peaks at around 40 eV before falling rapidly as $\ln (E) / E$ for all optically allowed transitions in accordance with the Bethe-Born Approximation [67]. In the literature we do not find any comparison for $\Sigma Q_{\text{exc}}$. Hence, this is the first attempt to report total excitation cross sections for all these astro-molecules.

For ready reference we present the numeric data of the total cross sections, $Q_{\text{ion}}$, $Q_{\text{el}}$ and $Q_T$ in table 4 and table 5.

### Table 4 $Q_{\text{ion}}, Q_{\text{el}}$ and $Q_T$ in Å² (±10-20 %)

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>Hydrogen cyanide (HCN)</th>
<th>Cyanoacetylene (HCCCN)</th>
<th>Vinyl cyanide (CH₂CHCN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Q_{\text{ion}}$</td>
<td>$Q_{\text{el}}$</td>
<td>$Q_T$</td>
</tr>
<tr>
<td>15</td>
<td>0.00</td>
<td>26.20</td>
<td>26.24</td>
</tr>
<tr>
<td>20</td>
<td>0.16</td>
<td>21.91</td>
<td>22.45</td>
</tr>
<tr>
<td>30</td>
<td>0.93</td>
<td>14.37</td>
<td>16.31</td>
</tr>
<tr>
<td>40</td>
<td>1.70</td>
<td>10.54</td>
<td>13.57</td>
</tr>
<tr>
<td>80</td>
<td>2.98</td>
<td>5.38</td>
<td>9.59</td>
</tr>
<tr>
<td>90</td>
<td>3.06</td>
<td>4.87</td>
<td>9.06</td>
</tr>
<tr>
<td>100</td>
<td>3.13</td>
<td>4.48</td>
<td>8.66</td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>Methanimine (CH$_2$NH)</td>
<td>Ethanimine (CH$_3$CHNH)</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$Q_{\text{ion}}$</td>
<td>$Q_{\text{el}}$</td>
<td>$Q_T$</td>
</tr>
<tr>
<td>15</td>
<td>0.14</td>
<td>25.65</td>
<td>26.21</td>
</tr>
<tr>
<td>20</td>
<td>0.73</td>
<td>19.79</td>
<td>21.57</td>
</tr>
<tr>
<td>30</td>
<td>2.07</td>
<td>14.03</td>
<td>17.87</td>
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<tr>
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<td>3.05</td>
<td>10.79</td>
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</tr>
<tr>
<td>90</td>
<td>4.14</td>
<td>5.29</td>
<td>10.71</td>
</tr>
<tr>
<td>100</td>
<td>4.11</td>
<td>4.91</td>
<td>10.17</td>
</tr>
<tr>
<td>600</td>
<td>1.85</td>
<td>1.99</td>
<td>3.91</td>
</tr>
</tbody>
</table>

Table 5 $Q_{\text{ion}}$, $Q_{\text{el}}$ and $Q_T$ in Å$^2$ (±10-20 %)
(B) Elastic cross sections

In this sub section we present our evaluation of the total elastic cross sections $Q_{el}$ and total cross sections $Q_T$ for these astro-molecules. We present our results graphically in figures 7 to 12. To the best of our knowledge there are no previous theoretical or experimental data for $Q_{el}$ or $Q_T$ for these molecules except for HCN and HCCCN.

For HCN we have shown present $Q_{el}$ in figure 7 along with theoretical data of Jain and Baluja [35] and Sanz et al [36]. While present $Q_{el}$ data display overestimation at lower energies, they show very good accord with Jain and Baluja [35] beyond 40 eV and with Sanz et al. [36] beyond 60 eV. Sanz et al [36] have used the screen corrected independent atom model (SC-IAM) that does not include molecular bonding and geometrical effects and is a good tool at higher energies typically beyond 30 eV [36]. We compare our $Q_{el}$ data with the results of Jain and Baluja [35] without the anisotropic term contributions and find reasonable agreement except at lower energies.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>$Q_{el}$ (mb)</th>
<th>$Q_T$ (mb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>1.66</td>
<td>1.83</td>
</tr>
<tr>
<td>800</td>
<td>1.51</td>
<td>1.70</td>
</tr>
<tr>
<td>900</td>
<td>1.39</td>
<td>1.59</td>
</tr>
<tr>
<td>1000</td>
<td>1.28</td>
<td>1.50</td>
</tr>
<tr>
<td>2000</td>
<td>0.73</td>
<td>0.97</td>
</tr>
<tr>
<td>3000</td>
<td>0.51</td>
<td>0.73</td>
</tr>
<tr>
<td>4000</td>
<td>0.39</td>
<td>0.60</td>
</tr>
<tr>
<td>5000</td>
<td>0.31</td>
<td>0.52</td>
</tr>
</tbody>
</table>
In figure 8 we show present $Q_T$ for HCN compared with previous theoretical results [35, 36, 37] and the experimental results of Srivastava et al. [32]. We observe that the present data show reasonable agreement with the results of Sanz et al. [36]. The theoretical data of Jain and Baluja [35] shows good agreement with the present results except at lower energies below 30 eV. This could be attributed to choice of different model potentials by them. For HCN, Srivastava et al. [32] have reported experimental differential cross sections using which, we have obtained $Q_T$. Srivastava et al. [32] reported measurements of the integral cross sections at 3 eV, 5 eV, 11.6 eV, 21.6 eV and 50 eV. Since the present data do not include non-spherical effects like rotational and vibrational processes we have subtracted the non-spherical cross sections reported by Sanz et al. [36] from integral cross sections of Srivastava et al. [32]. The two derived points with quoted uncertainty of 21 % do not agree with any of the theoretical data. De Heng et al. [37] have reported $Q_T$ from 100 eV-5000 eV. They overestimate the present data up to 500 eV, but thereafter agree with the present data following the Bethe Born trend [67].

In figure 9 we have shown present $Q_{el}$ for HCCCN as compared with the previous $Q_{el}$ data of Kaur et al. [39] along with the present $Q_T$ for which we have not found any experimental or theoretical results in literature. We find large differences for present $Q_{el}$ with the $Q_{el}$ values of Kaur et al [39] below 30 eV, after which the present cross sections show slightly lower values with expected nature of the curve.
Fig. 7 $Q_{el}$ for e-HCN scattering

Solid line: Present $Q_{el}$; Dash-Dot line: Jain & Baluja $Q_{el}$ [35]; Short Dash line: Sanz et al. $Q_{el}$ [36]

Fig. 8 $Q_T$ for e-HCN scattering


Fig. 9 $Q_T$ and $Q_{el}$ for e-HCCCN

Fig. 10 $Q_T$ and $Q_{el}$ for e-CH$_2$CHCN
In figure 10 we present the $Q_{el}$ and $Q_T$ for e-CH$_2$CHCN. We do not find any data of $Q_{el}$ or $Q_T$ in literature for this important molecule for comparison with present results in the current energy range. These cross sections values depend on target polarizability, number of electrons and other geometric parameters. Therefore these cross sections reflect the size of the molecule. At the peak
of inelastic cross sections ($E_p$) the contribution of $Q_{el}$ and $Q_{inel}$ to the total cross sections is 67% and 33% respectively. In figure 11 we show the $Q_{el}$ and $Q_T$ curves for e-CH$_2$NH scattering. Although, Wang et al. [40] have reported $Q_{el}$ for methanimine, they are at very low energies (0-10 eV) and are not shown here. $Q_{el}$ and $Q_{inel}$ contribute 55% and 45% to $Q_T$ at $E_p$. The total elastic and total cross sections for e-CH$_3$CHNH scattering are shown in figure 12. The upper curve shows $Q_T$ and the lower curve $Q_{el}$. The $Q_{el}$ are sensitive to the polarization potential. While its contribution to $Q_T$ is 58 %, the share of $Q_{inel}$ is 42 % to $Q_T$ at the $E_p$. The $Q_T$ values show the upper limit of the occurrence of all the e-molecule phenomena in the spherical approximation, a feature further elaborated in figure 13 in terms of relative cross sections.

![Diagram showing contribution of various total cross sections at peak of $Q_{inel}$](image)

**Fig. 13 Contribution of various total cross sections at peak of $Q_{inel}$**

In figure 13 we compare contribution of various total cross sections for e – CH$_2$NH collision at $E_p = 62$ eV which is the electron energy for maximum value of $Q_{inel}$. The total cross sections $Q_T$ cover all the spherical effects induced by electron collision. At the peak of inelastic cross sections the contributions from $Q_{el}$ and $Q_{inel}$ tend to be about equal [68]. In the present case $Q_{el}$ is
55% and $Q_{mel}$ is 45% of $Q_T$ at $E_p$. The total inelastic cross section consists of total ionization and summed total excitation cross sections and the $Q_{ion}$ is about 70% and $\sum Q_{exc}$ is 30% to $Q_{mel}$ at the peak of $Q_{mel}$. The present methodology provides all these cross sections under the same formalism. This renders consistency to the data.

CONCLUSION

We have reported theoretical results on various total cross sections, $Q_T$, $Q_{el}$, $Q_{mel}$, $Q_{ion}$ and $\sum Q_{exc}$ for interaction of electrons (~10 eV to 5000 eV) with important astro-molecules, hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH$_2$CHCN), methanimine (CH$_2$NH) and ethanimine (CH$_3$CHNH), compounds found in dense tholins of Titan. We have employed SCOP to evaluate $Q_{el}$, $Q_{mel}$ and $Q_T$ and used CSP-ic to compute $Q_{ion}$ and $\sum Q_{exc}$. We have also obtained $Q_{ion}$ using BEB method. Such studies provide a test-bed for prebiotic chemistry that evolved to develop life on Earth. Owing to toxicity and other experimental difficulties, not much previous work is reported for these important astro-compounds. These are the first reports of these cross sections except for HCN and HCCCN in this energy range. For HCN we found good agreement with other earlier data [33, 35] except for the inelastic data of Sanz et al. [36] which significantly overestimates these cross sections at lower energies. The present results of $Q_{el}$ and $Q_T$ for HCN find good accord with the compared theoretical results [35-37] except at lower energies. For HCCCN, while the present $Q_{ion}$ results underestimate the theoretical data [38, 39], present $Q_{el}$ show reasonable matching with Kaur et al [39] beyond 30 eV. The total ionization cross sections $Q_{ion}$ and the peak value $Q_{ion}$ (peak) are sensitive to the ionization potential (table 3). For all these compounds summed total excitation cross sections, $\sum Q_{exc}$ are reported for the first time in this work to the best of our knowledge.
Under the spherical approximation, the SCOP and CSP-ic methods are simple, reliable and accurate quantum mechanical methods for study of molecules irrespective of their size, shape and reactivity and provide estimates on various electron driven processes under the same formalism (figure 13). The requirement of spherically symmetric potential due to the use of partial wave analysis that prevents us to include rotational and vibrational effects along with the semi-empirical argument for the value of $R_p$ lead to uncertainty in the cross section values of the order of 10-20 % which is same as quoted in most experimental results. We hope these results will engender other studies, both experimental and theoretical.

Acknowledgement

Minaxi Vinodkumar acknowledges Department of Science and Technology (DST-SERB), New Delhi for financial support through the major research project (EMR/2016/000470).

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Highlights

Article reference: PSS_2018_133

Title: ELECTRON INTERACTIONS WITH ASTRO CHEMICAL COMPOUNDS

Yogesh Thakar, Rakesh Bhavsar, Mohit Swadia, Minaxi Vinodkumar, Nigel Mason, Chetan Limbachiya

- The paper deals with theoretical study of various electron induced phenomena for important astrochemical molecules which are relevant for chemistry in the tholins of Titan, the largest satellite of Saturn.

- The theoretical methods employed for this study are:
  1. Spherical Complex Optical Potential (SCOP) method
  2. Complex Scattering Potential-ionisation contribution (CSP-ic) method
  3. Binary-Encounter-Bethe (BEB) method

- Computed total cross sections on electron impact with hydrogen cyanide (HCN), cyanoacetylene (HCCCN), vinyl cyanide (CH_2CHCN), methanimine (CH_2NH) and ethanimine (CH_3CHNH) are reported for energies ~10 eV to 5000 eV, along with comparison wherever available.

- The reported electron impact total cross sections are total elastic cross sections $Q_{el}$, total inelastic cross sections $Q_{inel}$, total ionization cross sections $Q_{ion}$, total excitation cross sections $\sum Q_{exc}$ and total cross sections $Q_T$.

- We have employed SCOP to evaluate $Q_{el}$, $Q_{inel}$ and $Q_T$ and used CSP-ic to compute $Q_{ion}$ and $\sum Q_{exc}$. We have also obtained $Q_{ion}$ using the BEB method.