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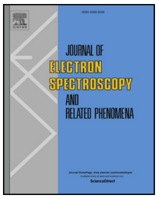

Electron impact ionization cross sections for methylamines

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ABSTRACT

Energy dependent single differential cross sections for the ionization of the $(CH_3)NH_2$, $(CH_3)_2NH$ and $(CH_3)_3N$ molecules by electron impact have been evaluated at fixed incident electron energy of 100eV. The modified Jain-Khare semiempirical formulation, which requires the oscillator strength data as input has been employed to calculate these cross sections. We have also derived integral total ionization cross sections in the electron impact energy range varying from ionization threshold to 1000 eV. The present total ionization cross sections reveal good agreement with the available only theoretical calculations from Spherical Complex Optical Potential (SCOP) and Binary Encounter Bethe (BEB) Formulations.

1. Introduction

Recently, we have employed the revisited Jain-Khare [1,2] semi-empirical formulation for the evaluation of energy dependent and total ionization cross sections for complex molecules [3–5] by electron impact. In the series of investigation, in the present work, we have chosen astrophysically relevant molecules viz. monomethylamine- $(CH_3)NH_2$, dimethylamine- $(CH_3)_2NH$, and trimethylamine- $(CH_3)_3N$. The study of electron impact ionization of molecules forms the essential basis for understanding the characteristics of the target molecules. The ionization cross sections are key parameters in the astrophysical study and modelling. Technologically, ionization cross sections for these molecules are important in processing plasmas [6,7].

In this work, we have evaluated the single differential ionization cross sections (SDCS) as a function of secondary/ ejected electron energy for methylamines at impinging electron energy 100 eV. The total ionization cross sections (TICS) in the incident electron energy range varying from ionization threshold to 1000 eV are also derived from SDCS. There is a very little study on electron/ photon scattering with the mono, di and tri methylamine molecules available on the experimental and the theoretical side which is striking contrast to the wealth of quantitative and qualitative information available for the parent member (NH_3) of this series. Photoionization of these molecules were measured using dipole (e,e) spectroscopy by Burton et al. [8] in the photon energy range from ionization threshold to 250 eV at low resolution (~1 eV fwhm) and to 31 eV at high resolution (0.048 eV fwhm). For electron impact ionization of these amines, no experimental data is available for cross sections. On the other hand, theoretically, few calculations for TICS are available for comparison of our calculated results viz. Spherical Complex optical Potential (SCOP) calculations by Vinodkumar et al. [9] for $(CH_3)NH_2$ and Binary Encounter Bethe (BEB) calculations for $(CH_3)_2NH$ and $(CH_3)_3N$ produced by Mozejko et al. [10,11]. In unavailability of single differential ionization cross sections (SDCS), the calculated TICS are in good agreement with the available theoretical data sets [9–11].

2. Theoretical

The detail of the present semiempirical model is described elsewhere [1–5]. In brief, the ionization cross section per unit energy range $Q_i(E,\varepsilon)$, for the production of a secondary electron of energy ε and a cation of ith type due to the ionization of a molecule by an electron of incident energy E is given by:

$$Q_i(E,\varepsilon) = \frac{4\pi a_0^2}{E}\left[\begin{array}{c}\frac{1}{\left(1+\frac{I_i}{E}\right)}\left(1-\frac{\varepsilon}{(E-I_i)}\right)\frac{R}{W}\frac{df_i(W,0)}{dW}\,ln(1+C_i(E-I_i)+\\ S_i\frac{(E-I_i)R}{(\varepsilon^3+\varepsilon_{0i}^3)}\left(\varepsilon-\frac{\varepsilon^2}{(E-\varepsilon)}+\frac{\varepsilon^3}{(E-\varepsilon)^2}\right)\end{array}\right] \tag{1}$$

Where *$df_i(W,0)/dW$* is the optical oscillator strength for the production of the ith type ion. ε_{0i}, C_i, R and I_i are the mixing parameter, collisional parameter, Rydberg's constant and ionization potential, respectively. W, the energy loss is the sum of ionization potential I_i and the secondary electron energy ε.

To obtain integral or total ionization cross sections for the production of the ith type of ion, for all the possible values of ε, we integrate Eq. (1) over ε from 0 to $(E\text{-}I_i)$ or over W from I_i to E.

$$Q_i(E) = \int_0^{(E-I_i)} Q_i(E,\,\varepsilon)\,d\varepsilon \tag{2}$$

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In the present formulation, the dipole oscillator strength df_i/dW is the key parameter and is directly proportional to the photoionization cross section [8] as

$$\sigma^{photo}_{(Mb)} = 109.75\frac{df_i}{dW}(eV)^{-1} \tag{3}$$

Where $\sigma^{photo}_{(Mb)}$ is the photoionization cross section in mega barn units.

We have used photoionization cross section data sets in the photon energy range from ionization threshold to 250 eV measured by Burton et al [8]. The accuracy of the determined oscillator strength scales was estimated to be better than ± 5%. For higher photon energy range W > 250 eV the same were extrapolated by Thomas-Reiche-Kuhn (TRK) sum rule, within ± 5% error bars [8]. However, its evaluation is possible quantum mechanically using the suitable wave functions and transition probabilities corresponding to the production of cations. In case of ionization of polyatomic molecule $(CH_3)NH_2$, $(CH_3)_2NH$ and $(CH_3)_3N$, we have no suitable wave functions and the transition probabilities corresponding to ionization processes. The collision parameters C_i and energy parameters $\mathcal{E}_{0i}$, evaluated as for other polyatomic molecules [1–5], along-with the vertical onsets or the ionization potentials corresponding to the formation of cations are presented in Table 1. In the present evaluations of cross sections, the total estimated uncertainty is approximately the same as in the measurement of photoionization cross sections. However, the same approach was employed for evaluation of TICS for molecules using several rigorous inputs as required in BEB calculations without any better accuracy [12].

3. Results and discussion

The CH_3NH_2, $(CH_3)_2NH$ and $(CH_3)_3N$ molecules belong to the groups of the highest symmetry C_s, C_s, and $C_{3\upsilon}$, respectively. In independent particle model (IPM), the ground state molecular orbital configurations are given as:

CH_3NH_2:

$(1a')^2$: N1s; $(2a')^2$:C1s; $\{(3a')^2\,(4a')^2\,(1a'')^2\,(5a')^2\,(6a')^2\,(2a'')^2\,(7a')^2\}$: Valence shell

$(CH_3)_2NH$:

$(1a')^2$: N1s; $\{(1a'')^2(2a')^2\}$:C1s; $\{(3a')^2(2a'')^2(4a')^2(5a')^2(6a')^2(3a'')^2(4a'')^2(5a'')^2(7a')^2(8a')^2\}$: Valence shell

$(CH_3)_3N$:

$(1a_1)^2$: N1s; $(2a_1)^2(1e)^4$:C1s; $\{(3a_1)^2(2e)^4(4a_1)^2(5a_1)^2(3e)^4(4e)^4(1a_2)^2(5e)^4(6a_1)^2\}$: Valence shell

The differential cross sections as a function of secondary electron energy at fixed incident electron energy of 100 eV are presented in the Fig. 1 along-with Table 2. To the best of our knowledge, no experimental and/or data is available to compare the present results. In the present formulation (Eq. (1)), the first part (Born-Bethe part) for slow secondary electrons, correspond to the growing contribution of the dipole-allowed interaction (known as glancing collision) and resembles the photo behaviour of the cross sections. Moreover, the cross sections are symmetrical about the W/2 wherein the energies of the incident and the secondary electrons are almost equal. The second part, accounts for the electron exchange effect, is non-dipole part, defines the knock-on-collision. Since, no data seems to exist for differential cross sections, the corresponding derived integral or total ionization cross sections from ionization threshold to 1000 eV, become important and are shown in the Fig. 2 with numeral values in Table 3. In this figure, we have presented the comparison of our ionization cross sections (TICS) with the established theoretical data sets: SCOP [9] and BEB calculations [10,11]. The calculated results for methylamines are in good agreement with the available only theoretical data sets within ~10% error bars. However, the peaks of the total ionization cross sections corresponding to the energy are slightly shifting in comparison to the other calculations. To the best of our knowledge, no experimental data for TICS is available for comparison.

Table 1
Table for calculated collision and energy parameters and ionization potentials for methylamine molecules.

Molecules	$C_i(eV^{-1})$	ε_{0i}(eV)	I_i(eV) [13,14]
$(CH_3)NH_2$	0.053	100	8.80
$(CH_3)_2NH$	0.051	75	8.24
$(CH_3)_3N$	0.048	100	7.82

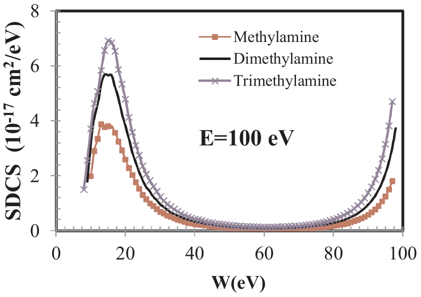

Fig. 1. Single differential cross sections (SDCS) as a function of secondary electron energy $\mathcal{E}$ ($W = I + \mathcal{E}$) for CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ by electron impact at E = 100 eV.

Table 2
Table for energy dependant/ single differential cross sections (SDCS) at impinging electron energy E = 100 eV.

W(eV)	$Q_i(E,W)(10^{-17}\,cm^2/eV)$		
	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
10	2.00	3.18	3.72
12	3.36	4.61	5.08
15	3.81	5.66	6.92
20	2.60	3.81	4.79
25	1.31	1.83	2.35
30	0.70	0.96	1.23
35	0.39	0.55	0.70
40	0.25	0.33	0.42
45	0.16	0.22	0.28
50	0.11	0.15	0.20
55	0.09	0.12	0.16
60	0.07	0.10	0.14
65	0.07	0.11	0.15
70	0.09	0.13	0.18
75	0.12	0.18	0.26
80	0.18	0.29	0.41
85	0.31	0.50	0.71
90	0.59	0.94	1.38
95	1.26	2.08	3.15

In the present situation, it is important to apply possible checks to the calculated data to access their consistency and reliability. It is clear that the areas covered in Fig. 1, for energy dependent single differential cross sections (SDCS), corroborate the ionization cross sections at 100 eV. A further consistency check can be applied for ionization cross sections. It is evident that the ionization cross sections are consistent with the other theoretical data.

$$Q_i(E) \sim E^m \tag{4a}$$

In the threshold regions, the presently evaluated integral cross sections obey the Wannier threshold law [15,16] where m is defined in terms of charge z on the residual ion.

$$m = -\frac{1}{4} + \frac{1}{4}\left(\frac{100z-9}{4z-1}\right)^{1/2} \tag{4b}$$

These consistency checks provide the consistency and reliability of our results.