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Cross-sections for electron–imidogen radical (NH) collisions

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Abstract

In this work, we report a theoretical study on electron collisions with NH radicals in the low and intermediate energy ranges. Calculated elastic differential, integral and momentum-transfer cross-sections as well as grand-total (elastic + inelastic) and total absorption cross-sections for electron–NH collisions are reported in the (1–500)-eV range. A complex optical potential composed by static, exchange, correlation–polarization plus absorption contributions, derived from a fully molecular wave function, is used to describe the interaction dynamics. The Schwinger variational iterative method combined with the distorted-wave approximation is applied to calculate scattering amplitudes. Present calculated results are compared with the existing data for electron–NH scattering in the literature. Also, comparison made between our calculated cross-sections for elastic scattering with the theoretical and experimental results for electron–NH_3 collisions has revealed remarkable similarity even at incident energies as low as 1 eV.

Keywords: Electron scattering; Imidogen; Cross-sections

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1. Introduction

Cross-sections for electron scattering from a variety of transient molecules such as free radicals are demanded in different fields of pure and applied sciences [1–3]. The imidogen (NH) free radical is one of such species. Imidogen plays a significant role in many chemical processes, including combustion [4–6]. NH was also identified in the plasma nitriding processes of materials using the N_2/H_2 mixture or ammonia [7]. The presence of NH in interstellar space was confirmed through transitions in its electronic, vibration–rotation, and high-N rotational spectra [8,9]. The knowledge of the abundance of NH in dark clouds is of importance for the study of nitrogen chemistry because it is likely an intermediate in the formation of NH_3 by successive hydrogenation reactions [10,11]. In addition, the abundance of nitrogen in planet-harboring stars can also be monitored via spectral synthesis of the near-UV NH band of 3360 Å [12].

In view of the above applications, the knowledge of the cross-sections for electron–NH collisions is certainly of interest. However, there is a lack of either experimental or theoretical studies on such matter in the literature. Due to its high chemical reactivity, it would be very difficult to generate a NH radical beam to be interacted with electron beam, thus experimental studies on electron–NH collisions would be a very hard task. To our knowledge, there is only one article [13] that reports the measurement of total ionization cross-sections (TICSs) for electron-impact on ND, an isotopic substitute of NH. Theoretically, studies on electron–NH scattering are equally scarce. In 2001, total cross-sections (TCSs) and total absorption cross-sections (TACSs), and estimated TICSs for electron–NH collisions in the 10–2000 eV range were calculated by Joshipura et al. [14] using the additivity rule. In their calculations, complex optical potentials were used to represent the interaction between the scattering electron with N and H atoms. Due to the simplicity of the method, the additive rule is expected to fail at incident energies below 100 eV.

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In this work, we present a theoretical study on electron–NH scattering covering a wide incident energy range. More specifically, DCSs, integral (ICSs) and momentum transfer (MTCSs) cross-sections for elastic e^-–NH scattering as well as TCSs and TACSs in the (1–500)-eV energy range are calculated and reported. The present study made use of a complex optical potential to represent the electron–radical interaction whereas a combination of the Schwinger variational iterative method (SVIM) [15,16] and the distorted-wave approximation (DWA) [17–19] is used to solve the scattering equations.

The organization of this paper is as follows. In Section 2, we describe briefly the theory used and also some details of the calculation. In Section 3 we present our calculated results.

2. Theory and calculation

Details of the SVIM [15,16] and the DWA [17–19] have already been presented previously, and will only be outlined here.

Since NH is an open-shell target, the coupling of the incident electron with the two unpaired 1π electrons of the target leads to two spin-specific scattering channels, namely, the doublet ($S=1/2$) and quartet ($S=3/2$) couplings. At the fixed equilibrium internuclei distance and using the adiabatic-nuclei-rotation (ANR) approximation, the rotational-transition scattering amplitude for a specific spin-coupling is given as

$$f^S_{jm_j\leftarrow j_0m_{j_0}} = \langle jm_j|f^S|j_0m_{j_0}\rangle, \tag{1}$$

where $|jm_j\rangle$ are the rigid-rotor wave functions and $f^{(S)}$ the spin-specific fixed-nuclear electron scattering amplitude in the laboratory-frame (LF). Accordingly, the spin-specific DCSs for the rotational excitation from an initial level j_0 to a final level j is given by

$$\left(\frac{d\sigma}{d\Omega}\right)^S (j\leftarrow j_0) = \frac{k_f}{k_0}\frac{1}{(2j_0+1)}\sum_{m_jm_{j_0}}|f^S_{jm_j\leftarrow j_0m_{j_0}}|^2, \tag{2}$$

where k_f and k_0 are the final and initial linear momenta of the scattering electron, respectively.

Moreover, the spin-specific rotationally unresolved DCSs for elastic e^-–NH scattering are calculated via a summation of rotationally resolved DCSs

$$\left(\frac{d\sigma}{d\Omega}\right)^S = \sum_{j=0}\left(\frac{d\sigma}{d\Omega}\right)^S (j\leftarrow j_0). \tag{3}$$

Finally, the spin-average DCSs for elastic e^-–NH scattering is calculated using the statistical weight for doublet (1/3) and quartet (2/3) scattering channels, as

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{1}{3}\left[\left(\frac{d\sigma}{d\Omega}\right)^{S=1/2} + 2\left(\frac{d\sigma}{d\Omega}\right)^{S=3/2}\right]. \tag{4}$$

In the present study, the electron-molecule scattering dynamics is represented by a complex optical potential

$$V_{\text{opt}}(\vec{r}) = V^{\text{SEP}}(\vec{r}) + iV_{\text{ab}}(\vec{r}), \tag{5}$$

where the V^{SEP} is the real part of the interaction potential composed by the static (V_{st}), the exchange (V_{ex}) and the correlation–polarization contributions (V_{cp}) whereas V_{ab} is the absorption potential. In our calculation, V_{st} and V_{ex} are derived exactly from a restricted open-shell Hartree–Fock (ROHF) self-consistent-field (SCF) target wave function. A parameter-free model potential introduced by Padial and Norcross [20] is used to account for the correlation–polarization contributions. In this model, a short-range correlation potential between the scattering and target electrons is defined in an inner interaction region and a long-range polarization potential in an outer region. The first crossing of the correlation and polarization potential curves defines the inner and outer regions. The short-range correlation potential is derived using the target electronic density according to Eq. (9) of Padial and Norcross [20]. In addition, an asymptotic form of the polarization potential is used for the long-range electron–target interactions. The application of this model requires dipole polarizabilities to generate the asymptotic form of V_{cp}. Since there is no experimental and/or theoretical values available in the literature for the NH radical, they were calculated in this work at ROHF level of approximation. The calculated values are $\alpha_{zz}=11.339$ a.u. and $\alpha_{xx}=7.802$ a.u. No cut-off or other adjusted parameters are needed in the calculation of V_{cp}.

Although the main features of the absorption effects are known, taking these effects into account in an ab initio treatment of electron-molecule scattering is very difficult. Presently, despite the ab initio methods (e.g. *R*-matrix [21], Kohn variational [22], and Schwinger multichannel [23], etc.) are routinely applied to electron-molecule collisional studies, these applications are in general limited in the low incident energy range (≤ 30 eV) where the absorption effects are absent or small. In order to treat the absorption effects, those methods of close-coupling nature would require all discrete and continuum open channels to be included in the open-channel P-space, which are still computationally unfeasible. In view of the difficulties, the use of the model absorption potential seems to be presently the only practical manner to account for absorption effects into electron-molecule scattering calculations. Several model absorption potentials have been proposed and used, but the version 3 of the quasifree scattering model (QFSM) proposed by Staszewska et al. [24], and lately modified by Jain and Baluja [25], has shown to yield cross-sections in better agreement when compared with experiments. We have chosen the latter to account for the absorption component of the electron–radical interaction potential.