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LOW ENERGY ELECTRON IMPACT CALCULATION FOR N_2O SCATTERING

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ABSTRACT

Comprehensive computation of electron impact total cross sections (Q_T) is carried out for e-N_2O scattering for low impact energies from 0.01 eV to 20 eV. We employ an ab initio calculation using R-Matrix formalism. Total cross section is obtained as sum of total elastic and total electronic excitation energy. A good amount of literature is available and hence fruitful comparisons were made and overall good agreement is observed with available theoretical as well as experimental results.

Key Words: *R-matrix method, Ab initio calculations, elastic cross section, excitation cross section, nitrous oxide*

INTRODUCTION

Investigation of electron collision with nitrous oxide (N_2O) has been the topic of interest recently due to its presence in various environments and its chemistry in these environments. The presence of N_2O in earth's upper atmosphere and its reaction with ozone molecules and hence the destruction of the ozone layer has been one of the motivation behind the studies on N_2O molecule. Besides, electron scattering data with nitrous oxide is also important in the study of plasma physics, laser physics and interstellar atmosphere models [1]. It is also used in medicine as anesthetic and in the technological processes having cold plasma [2, 3].

Low energy electron impact scattering studies on N_2O have been done by many experimental and theoretical groups. In the experimental front we have Kitajima et al [2], Kwan et al [4], Strakeljahn et al [5] and Marinkovic et al [3]. There are quite a good number of theoretical calculations on this molecule as well. Michelin et al [6] have used Born-closure Schwinger variational method to find the total cross section, Tennyson and Morgan [1] and Sarpal et al [7] have employed R-matrix method and Winstead and McKoy [8] have used Schwinger multichannel (SMC) method to find cross sections. A comprehensive list of previous attempts to measure or calculate cross section of electron scattering by N_2O is given in Table 1. Even though there are quite a good number of literatures available on N_2O, the interest on this molecule has never diminished due to its presence in various natural and industrial environments and its chemistry with other constituents of the environment. In the present work our aim is to calculate total cross section for electron impact on N_2O gas and validate it against the existing data. For this purpose we have used the *ab-initio* R-matrix calculations through Quantemol-N software [8]. A detailed description on the theoretical methodology adopted is given in the next section.

Measurements	**Ref.**	**Theory**	**Ref.**
Kitajima et al (DCSs)	[2]	Tennyson and Morgan	[1]
Kwan et al (TCS)	[4]	Michelin et al	[6]
Strakeljahn et al (TCS)	[5]	Winstead and McKoy	[9]
Marinkovic et al (elastic)	[3]	Morgan et al	[16]
Zecca et al (TCS)	[10]	Azria et al (excitation)	[17]
Szmytkowski et al (TCS)	[11,12]	Tronc et al (excitation)	[18]
Johnstone and Newell (elastic)	[13]	Andrick and Read (excitation)	[19]
Andric and Hall (excitation)	[14]	H. Kato et al	[20]
Akther et al (DCSs)	[15]	Joshipura et al	[21]
Kawahara et al both theory & exp (excitation)			[22]

THEORETICAL METHODOLOGY

This paper reports low energy (0.01eV to about 20 eV) *ab-initio* calculations using Quantemol-N [23] employing UK molecular R-matrix code [24]. For the low energy calculations the target model plays an important role as its correct representation ensures accuracy in the calculation. Before going to the details of theoretical method we discuss the target model employed for the present systems.

A. Target Model

N_2O is a linear molecule with center nitrogen atom bonded by double bond with other nitrogen atom (2.13 au) and oxygen atom (2.23 au) [25]. In present formalism we have used the Gaussian basis set 6-311G. Here 6 gaussians are used to sum up inner shell orbitals, 3 gaussians for the first Slater type orbitals (STO) of the valence orbitals and 1 gaussian for the second and third STO of the valence orbitals. N_2O has $C_{\infty v}$ point group symmetry but we have considered C_{2V} point group symmetry of the order 4 as it reduces the computational efforts that are required to generate the target wave function. The ground state Hartree-Fock electronic configuration is $1a_1^2\, 2a_1^2\, 3a_1^2\, 4a_1^2\, 5a_1^2\, 6a_1^2\, 1b_1^2\, 1b_2^2\, 7a_1^2\, 2b_2^2\, 2b_1^2$. Out of 22 electrons we have frozen 6 electrons in $1a_1$, $2a_1$, $3a_1$ molecular orbitals while remaining 16 electrons are kept free in active space of $4a_1$, $5a_1$, $6a_1$, $7a_1$, $1b_1$, $2b_1$, $3b_1$, $1b_2$, $2b_2$, $3b_2$ molecular orbitals. Total 28 target states are represented by 1081 configuration state functions (CSF's) for the ground state and number of channels included in the calculation is 171. This large number of CSFs ensures the correct determination of resonance peaks particularly in the low energy regime. The R-matrix radius is taken as 10 au while R-matrix calculation is propagated up to 100.1 au. The GAUSPROP and DENPROP modules [26] yield the ground state energy of -183.71 Hartree which is in very good agreement with -183.75 Hartree [27], -183.69 Hartree [7] and -183.74 Hartree [30], -184.16 Hartree [7] predicted earlier. The first electronic excitation energy is 5.86 eV which is probably reported for the first time. N_2O is weakly polar molecule. The present computed dipole moment is 0.15 au which is in good agreement with measured value 0.16 au predicted by Lovas [28] and comparable with 0.18 au predicted by Sarpal et al [7] and 0.18 au predicted by Mechlinska et al [29]. The dipole moment predicted by Winstead and Mc Koy, Mechlinska et al and Michelin et al [9, 29, 6] is around 0.63 au, 0.64 and 0.68 au respectively which are very high compared to present and

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Target	Ground state energy (Hartree)		Dipole moment (au)			First excitation energy E_1 (eV)		Rotational Constant (B) (cm^{-1})	
	Present	Theo	Present	Theo	Exp	Present	Theo	Present	Theo
N_2O	-183.71	-183.69[6] -183:75[27] -183.73[9] -183.74[29]	0.15	0.184[29] 0.68[6] 0.64[28] 0.63[9] 0.18[7]	0.16[28]	5.86	-	0.421	0.419[25]

Table 1. Target Properties: Ground state energy (Hartree), Dipole moment (au), First electronic excitation energy (eV) and Rotational constant (cm^{-1}).

experimental value of Lovas [28]. The present rotational constant of 0.4211cm^{-1} is in very good agreement with theoretical value 0.4190 cm^{-1} reported in [25]. All the computed target parameters for N_2O are reported in Table 1 with available comparisons.

The electronic excitation thresholds for N_2O are listed in Table 2. Here $^3A_1$ and $^1A_2$, $^1B_1$ and $^1B_2$, $^1A_2$ and $^1A_1$, and $^1A_2$ and $^1A_1$ are degenerate states having energies 6.486 eV, 7.134 eV, 11.357 eV and 12.636 eV respectively. N_2O has total 16 electronic excitation states.

Table 2. Vertical excitation energies of N_2O in eV.

State	**Energy**	**State**	**Energy**	**State**	**Energy**
$^1A_1$	0.0	$^3B_1$	9.836	$^1A_2$	7.134
$^3A_1$	5.866	$^1B_2$	11.357	$^3B_1$	9.836
$^3A_1$	6.486	$^3A_1$	11.556	$^1A_1$	12.636
$^3A_2$	6.818	$^1A_2$	11.953	$^3A_1$	13.422
$^1A_2$	7.025	$^3A_2$	12.279	-	-
$^1A_2$	7.134	$^1A_2$	12.513	-	-

Low energy formalism (0.01 eV -20 eV)

The main goal behind the R-matrix formulation [26] lies in dividing the complete configuration space into two spatial regions termed as inner region having R-matrix radius of ~10 au and the outer region extending to the radius of 100 au. The inner region is a sphere whose center coincides with the center of mass of the target molecule and whose radius is so chosen that all N+1 electrons (N target electrons+1scattering electron) lies within the sphere. Moreover the splitting of R-matrix configuration space into these two regions also relies on the size of the target and on the stability of the results obtained in the inner region and outer region calculations. This distribution is the consequence of electronic charge distribution around the center of mass of the system. Presently we have considered R-matrix radius as 10 au for N_2O which was found to give consistent results.

The main task in the present scattering calculation lies in the solution of time independent Schrodinger equation. For this we construct the wavefunction for the inner region using close coupling approximation [31] given by,

$$\psi_k^{N+1} = A\sum_I \psi_I^N (x_1,\cdots,x_N) \sum_j \zeta_j (x_{N+1}) a_{Ijk} + \sum_m \chi_m (x_1,\cdots,x_{N+1}) b_{mk} \tag{1}$$

where A is the anti-symmetrization operator obtained by imposing Pauli's exclusion principle on the target plus scattering electrons, x_N is the spatial and spin coordinate of the nth target electron, ξ_j is a continuum orbital spin-coupled with the scattering electron and a_{Ijk} and b_{mk} are variational coefficients determined by the diagonalization of Hamiltonian matrix.

The first summation runs over the target plus continuum states used in the close-coupled expansion. The second summation runs over configurations χ_m, where all electrons are placed in target molecular orbitals. The number of these configurations varies considerably with the model employed. With the wavefunction given by eqn. (1), a static exchange calculation has a single Hartree-Fock target state in the first sum. The second sum runs over the minimal number of configurations usually 3 or fewer, required to relax orthogonality constraints between the target molecular orbitals and the functions used to represent the configuration. Our fully close-coupled calculation uses the lowest number of target states, represented by a configuration interaction (CI) expansion in the first expansion and over a hundred configurations in the second. These configurations allow for both orthogonality relaxation and short-range polarization effects.

The complete molecular orbital representation in terms of the target and the continuum orbitals is done by using the Gaussian Type Orbitals (GTOs) and the molecular integrals are generated by the appropriate Molecular Package. The R-matrix will provide the link between the inner region and outer region. For this purpose the inner region is propagated to the outer region potential until its solutions match with the asymptotic functions given by the Gailitis expansion [32]. Thus by generating the wave functions, using equation 1, their eigen values are determined. These coupled single center equations describing the scattering in the outer region are integrated to identify the K-matrix elements. Consequently the resonance positions, widths and various cross sections can be evaluated using the T-matrix obtained from S-matrix which is in turn obtained by the K-matrix elements.

RESULTS AND DISCUSSION

The present low energy *ab initio* calculations are carried out using R-matrix code employing Quantemol-N package. The calculations are carried out using the fixed-nuclear static-exchange-polarization approximation at the equilibrium geometry of the ground-state N_2O.The main incentive of present work is twofold, one to detect the resonance structure at low energies and second to compare present results with available data. The numerical results of total cross section are tabulated in Table 3 and also shown graphically vide figures 1-2. For clarity of Figures we have compared present results separately with theoretical and experimental results.

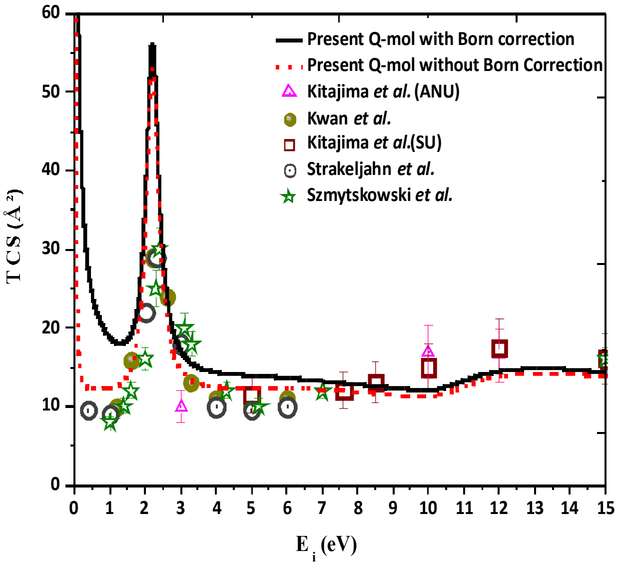

Figure 1: (Colour online) Comparison of present TCS for e-N$_2$O scattering with experimental results.

Solid line: Present results (Q-mol with Born correction); Square: Kitajima et al (ANU) [2]; Triangle: Kitajima et al (SU) [2]; Circle: Kwan et al [4]; Diamond: Strakeljahn et al [5] and Stars: Szmytkowski et al [11].

In Figure 1 present TCS is compared with the available experimental integral elastic results of Kitajima et al [2] and total cross section results Kwan et al [4], Strakeljahn et al [5] and Szmytkowski et al [11]. Present data are qualitatively in agreement with all the measurements and show similar structure. The position of the peak is found to be around 2.23 eV which is consistent with measurements Kwan et al [4], Strakeljahn et al [5] and Szmytkowski et al [11]. The experimental results are in general found to be about 10-15% lower than the present data near the valley. This is attributed to two reasons, first being the measurements represent integral elastic cross sections (derived from DCS) [2] which excludes the contributions coming from inelastic channel and second at low energies and particularly at forward angles the extrapolation is done largely 'by eye' or some numerical fit which introduces error of about 25% [2]. Another fact is that here we have employed fixed nuclei approximation method meaning that vibrational and rotational channels are not considered in the calculation. If the vibrational channel is considered then the peak of the cross section will decrease as well as it will broaden the peak. However, on the higher energy region the measurement results increases rapidly to match with our values. The experimental values also show the hump at around 12 eV as shown by present results in Figure 1. In general, the trend demonstrated by our theoretical data is in very much accord with the experimental results.

Figure 2 shows the comparison of present data with available theoretical data [1, 6, 7, 9]. In general, there is a qualitative agreement between our calculated TCS in terms of position of the peak, maximum value of cross sections as well as shape of the curve with available theoretical data [1, 7, 9]. Quantitatively, however, at some incident energies the agreement is good whereas at some other energy, some discrepancies between the present calculated and other theoretical results are seen. For instance the present results are in very good agreement with results of Tennyson and Morgan [1] throughout the range. The present results are also in good agreement with calculations of Winstead and McKoy [9] and Sarpal et al [7] particularly in the peak range, below and above which there is some discrepancy. These may be attributed to difference in selection of target model and consequently the wavefunction. Results of Michelin et al [6] are very high compared to all results due to neglect of polarization effect and overestimation of DCS value in this angular region [6]. Below the resonance energy, the cross section at first decreases and then increases abruptly due to efficient scattering of very slow electrons by the dipole potential. Thus, this behavior should result into a minimum which is observed in present case at 0.38 eV which is in accordance with earlier theoretical predictions [1, 7, 8]. The upward turn is not observed in the results of Winstead & McKoy [8] due to neglect of long-range dipole interaction. The location of 2Σ resonance is sensitive to the polarization effect, it occurs at 10.5 eV in present calculation, 11 eV in the calculation of Morgan et al [15] who took into account the polarization effect and 13 eV in the calculation of Winstead & McKoy [8] who employed Static Exchange (SE) approximation. The steep rise in the present TCS curve and of Tennyson and Morgan [1] at low energy is due to polar nature of the molecule which arises due to permanent dipole moment of 0.15 au.

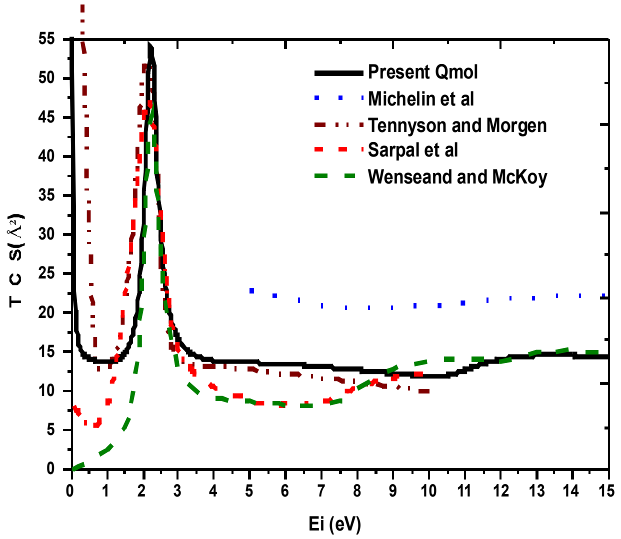

Figure 2: (Colour online) Comparison of present TCS for e -N$_2$O scattering with other theoretical results.

Solid line: Present results (Q-mol with Born correction); Dot: Michelin et al [6]; Dash-dot-dot: Tennyson and Morgan [1]; Dash-dot: Sarpal et al [7] and Dash: Winstead and McKoy [9].

Table 3: Total Cross Section Q_T(Å^2) for N_2O

E_i (eV)	TCS (Å^2)	E_i (eV)	TCS (Å^2)
0.01	141.52	3.01	16.57
0.05	33.65	3.51	14.40
0.11	20.48	4.01	13.90
0.21	16.09	4.51	13.72
0.31	14.89	5.01	13.65
0.41	14.41	6.01	13.46
0.51	14.15	7.01	13.13
1.01	13.77	8.01	12.72
1.51	14.93	9.01	12.28
2.01	31.20	10.01	11.89
2.15	48.53	11.01	12.72
2.23	54.14	12.01	14.07
2.30	49.57	13.01	14.58
2.35	45.07	14.01	14.57
2.51	29.06	15	14.28

CONCLUSION:

Low energy electron impact *ab initio* calculations on N_2O molecule were carried out using R-matrix code employing Quantemol-N package. The formalism has assumed a fixed-nuclear static-exchange-polarization approximation at the equilibrium geometry of the ground-state N_2O. The results are then compared with the available experimental and theoretical data and qualitatively and quantitatively good agreement is observed except at resonance region. This molecule is present in earth's upper atmosphere, atmosphere of other planets and interstellar media. It is also an important gas used in cold plasma and in medicine as anesthetic. Due to its importance in applied fields as mentioned, it has been studied comprehensively by both experimentalists and theoreticians. However, as depicted in the Figure 2, the theoretical values differ quite considerably. All these factors have prompted us to venture in to the calculation of electron impact cross section for this molecule. We are confident that present values are very reliable and can be used for further modeling in atmospheric studies as well as in technological plasmas.

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