Journal of Electron Spectroscopy and Related Phenomena 191 (2013) 71–78

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Electron scattering studies of nitrogen dioxide

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ARTICLE INFO

Article history:
Received 17 September 2013
Received in revised form 29 October 2013
Accepted 29 October 2013
Available online 6 November 2013

Keywords:
Nitrogen dioxide
R-matrix method
SCOP formalism
Dissociative electron attachment
Total cross section

ABSTRACT

Present work reports total cross sections for e-NO_2 scattering over an extensive range of impact energy from 0.5 eV to 2000 eV, through a composite formalism. The *ab initio* *R*-matrix method is employed for calculations up to 15 eV while the spherical complex optical potential formalism is used beyond that energy. The electronic excitation cross sections are computed from ground state X^2A_1 to seven electronically allowed excited states $^2B_1$, $^2B_2$, $^2A_2$, $^4A_2$, $^4B_2$, $^4A_1$, $^4A_1$ and $^4B_1$. The eigenphase diagrams presented here reproduces the resonances identified earlier. The structures detected at 1.33, 3 and 8.41 eV can be associated with the observed O^- anion formation through dissociative electron attachment process.

1. Introduction

Nitrogen dioxide (NO_2) is a toxic gas with a pungent unpleasant odour. It is considered as an atmospheric pollutant due to its involvement in reactions which produce ground-level ozone, and hence act as a precursor to smog. It can be easily converted into gaseous nitric acid and other organic nitrates in air, which are highly toxic. Nitrogen dioxide being the parent molecule to nitrates, contribute to irrespirable particle levels in the atmosphere. Even though the direct global warming potential of NO_2 is not a major issue, its indirect effects have been of great concern [1]. There are emissions of gases having negligible direct greenhouse effect, but are indirectly affecting the climate through impacting on chemical and physical processes in the atmosphere. Hence, such gases play crucial role in the chemistry of these atmospheres [2]. Also, the chemical lifetime of these species is mainly subject to short-lived gases in the troposphere. Although, they have negligible radiative effects in the wavelength range important for the climate modelling, these atmospheric compounds are very reactive and are found to affect the climate 'indirectly' through its contribution to the total radiative forcing [3].

The electron impact scattering of NO_2 molecule has been extensively studied, specifically at intermediate to high energies, however at low impact energies below 12 eV relatively little works have been reported as evident from the Table 1. Munjal et al. [4] have performed calculations using the *R*-matrix method to find elastic cross section at energies below 12 eV, while Curik et al. [5] employed a single centre approach in the energy range from 1 to 20 eV. Szmytkowski et al. [6] have measured the e-NO_2 cross section for energies in the range 0.6–220 eV through linear transmission technique. Later, Szmytkowski and Mozejko [7] repeated the experiment for the energy range 3–370 eV. Shi et al. [8], Sun et al. [9] and Zecca et al. [10] used the additivity rule (AR) to calculate the total cross section at intermediate to high energies. Prior to AR calculation, Zecca et al. [11] measured the total cross sections for e-NO_2 scattering for the energy range 90–4000 eV by attenuation method.

Hence, it is clear that a great deal of work has been done on this molecule due to its interest to atmospheric science. However, there exist clear discrepancies between various methods, especially below 100 eV. In this work we have reported the cross section data over extensive energy range from 0.5 to 2000 eV. In addition to cross sections, the present work investigated the formation of short-lived anions at low energy (<10 eV) in terms of resonances. Resonance leads to the decay of the molecule into neutral and negatively charged fragments, thus providing information on the dissociative attachment. These data are imperative in the understanding of electron interaction with targets, which determines the local chemistry of any atmosphere. In this work we have used the molecular *R*-matrix code through Quantemol-N package [12] to calculate the cross sections at low energies (below 15 eV). To obtain the cross sections above the ionization threshold the spherical complex optical potential (SCOP) formalism [13,14] is employed. In the next section we briefly describe the theoretical methods employed here to calculate the cross sections.

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http://dx.doi.org/10.1016/j.elspec.2013.10.010

Table 1
Literature survey for e-NO_2 scattering.

Energy range (eV)	References	Method (Exp—experimental; Th—theoretical)
0.5–12	Munjal et al. [4].	*R*-matrix (Th)
1–20	Curik et al. [5].	Single centre approach (Th)
0.6–220	Szmytkowski et al. [6].	Linear transmission technique (Exp)
3–370	Szmytkowski and Mozejko [7]	Linear transmission technique (Exp)
30–5000	Shi et al. [8].	Additivity rule (Th)
100–1600	Sun et al. [9].	Additivity rule (Th)
50–5000	Zecca et al. [10].	Additivity rule (Th)
90–4000	Zecca et al. [11].	Attenuation (Exp)

2. Theoretical methodology

We have employed two distinct formalisms in two prime energy regimes viz. low energy (<15 eV) and intermediate to high energy (16 to 2000 eV). For the low energy calculations, the *ab initio* R matrix method and for intermediate to high energy range SCOP formalism are employed. These methods will be discussed in the subsections 2.2 and 2.3. Before going into the details of the theoretical formalisms, the target model employed for the present calculations are explained below.

2.1. Target model used for low energy calculations

NO_2 is a trigonal planar molecule with bond angle of 134.2°. The central Nitrogen atom is bonded with one of the oxygen atom by double bond and with other oxygen atom by a single bond of identical bond length 2.25 au [15]. In order to generate accurate collision data it is required to have correct representation of the target wave function. The double zeta plus polarization (DZP) Gaussian basis set is used to construct the target wave function. This choice of the basis set is made such that the self consistent field calculations yield the best target properties. The calculations are done using C_{2V} point group symmetry of the order 4 which is the natural point group symmetry of NO_2 molecule. NO_2 being an open shell system, the restricted open shell Hartree–Fock (ROHF) wavefunction is employed to represent the target. The ground state Hartree–Fock electronic configuration of NO_2 molecule is $1a_1^2\ 2a_1^2\ 1b_2^2\ 3a_1^2\ 2b_2^2\ 4a_1^2\ 5a_1^2\ 3b_2^2\ 1b_1^2\ 4b_2^2\ 1a_2^2\ 6a_1^1$. Out of 23 electrons, we froze 6 electrons in $1a_1$, $2a_1$ and $1b_2$ molecular orbitals while the remaining 17 electrons are kept free in active space of $3a_1$, $4a_1$, $5a_1$, $6a_1$, $7a_1$, $1b_1$, $2b_1$, $2b_2$, $3b_2$, $4b_2$, $1a_2$ molecular orbitals. In this calculation, the target molecular orbital space is divided into core (inactive), valence (active), and virtual orbitals. These target molecular orbitals are supplemented with a set of continuum orbitals, centred at the center of mass of the molecule. A total of eight electronic excited target states are represented by 1391 configuration state functions (CSFs) for the ground state and the number of channels included in the calculation is 25.

The GAUSPROP and DENPROP modules [16] yield a ground state energy of −204.15 hartree which is in excellent agreement with the theoretical values of −204.07 hartree given by Munjal et al. [4], −204.06 hartree given by Curik et al. [5], −203.94 hartree reported by Fink [17] and −204.05 hartree given by Jackels and Davidson [18]. The present first electronic excitation energy is 3.01 eV which agrees well with the experimental value of 3.02 eV reported by Lievin et al. [19] and theoretical value of 3.08 eV predicted by Munjal et al. [4]. NO_2 is a weakly polar molecule. The present computed dipole moment is 0.5 D which is close to the theoretical values of 0.45 D predicted by Munjal et al. [4] and Jackels and Davidson [18] and slightly higher compared to 0.316 D reported by Leonardi et al. [20] and 0.33 D predicted by Curik et al. [5]. The present rotational constant of 7.99 cm^{-1} is in agreement with the experimental value 8.0 cm^{-1} reported in the computational chemistry comparison and benchmark database [15]. All the computed target parameters for NO_2 are reported in Table 2 with available comparisons. The comparison of the present target properties for NO_2 with available theoretical and experimental results reflect the fact that the basis set and hence the wave functions used in present calculations are reasonable and of good quality to produce reliable cross section data.

Table 3 summarizes the vertical excitation energies for the doublet and quartet states of NO_2 computed using the configuration integration (CI) model with available comparisons. The excitation energy of $^2B_1$ with present method is 3.01 eV which is in very good agreement with 3.02 eV of Lievin et al. [19] obtained using the complete active space self consistent field (CASSCF) method and 3.08 eV of Munjal et al. [4] obtained using the CI model. Similarly

Table 3
e–NO_2 vertical excitation energies for all states below the ionization threshold.

State	Present Energy (eV)	Munjal et al. [4]	Lievin et al. [19]	Gillispie et al. [21]
$^1A_1$	0.0	0.0	0.0	0.0
$^2B_1$	3.01	3.08	3.02	–
$^2B_2$	4.07	4.03	3.43	–
$^2A_2$	4.15	4.07	–	3.40
$^4A_2$	4.97	4.99	–	4.70
$^4B_2$	5.04	5.04	–	4.60
$^4A_1$	9.01	–	–	–
$^4B_1$	9.37	9.29	–	–

Table 2
Target properties obtained for the e-NO_2 molecule.

Properties of NO_2	Present	Experimental	Theoretical
Ground-state energy (hartree)	−204.15	–	−204.07 [4] −204.06 [5] −203.95 [17] −204.05 [18]
First excitation energy (eV)	3.01	3.02 [19]	3.08 [4]
Rotational constant (cm^{-1})	A−7.990 B−0.436 C−0.413	8.00 [15] 0.433 [15] 0.410 [15]	
Dipole moment (D)	0.50	0.316 [20]	0.33 [5] 0.45 [4] 0.45 [18]