Total relative differential cross section for 500-eV and 1-keV electrons scattered by nitrogen (N_2)†

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We measured total relative differential cross sections for electron collisions with molecular nitrogen. Results are presented between 6°–80° with 500-eV electrons and 2°–90° with 1-keV electrons. Theoretical calculations were also done utilizing partial waves for elastic channel and the Born approximation for the total inelastic cross section. In both cases use was made of Hartree-Fock-Clementi wave functions. The agreement between our theoretical and experimental results is analyzed, demonstrating the possibility of determining molecular-structure parameters at 1 keV.

I. INTRODUCTION

Since 1927 much effort has been made to measure differential cross sections (DCS) for scattering of low-[1–27] (below several hundred eV) and high-energy[28–30] (above 15 keV) electrons from atoms and molecules in the gas phase. Although most of the low-energy work found in the literature is concerned with electron impact spectroscopy and assignments of energy levels, those above 15 keV (especially between 40 and 60 keV) are mainly directed to determine the molecular parameters[30] through gas-phase electron diffraction.

In spite of the great interest of investigators in these two limits of energy, practically no work[11,19] can be found in the interval between 1 and 15 keV, which in further discussion we shall refer to as the medium-energy range. Although electrons with medium energy participate in many natural phenomena, and therefore some data in this range can eventually help to clarify some points of interest,[31] our initial interest is to determine the validity of some approximations,[32] used in gas-phase electron diffraction for high-energy electrons, when applied to the lower portion of the medium-energy range; these data are especially important for a better understanding of intramolecular multiple scattering[33–41] and its possible implications for the determination of molecular parameters by gas-phase electron diffraction.

In the following parts of this work we will describe our apparatus and the theoretical calculations used to interpret our measurements of the total (elastic plus inelastic) differential cross section (TDCS) for the nitrogen molecule with electrons of 500 eV and 1 keV.

II. EXPERIMENTAL

A schematic representation of the apparatus utilized in this work for the measurements of the TDCS reported here is seen in Fig. 1. It consists basically of a scattering chamber constructed of a nonmagnetic aluminum alloy coupled to a Varian VHS-6 diffusion pump and a 1397 Welch mechanical pump. The main body of the chamber is a cylinder 60 cm in diameter and 30 cm high, one flange in each side. The pumping system is separated from the scattering chamber by a cryosphere which can hold 9 liters of liquid nitrogen. In addition to these pumps one cryopump located in the upper flange contributes to the pumping speed of the system. With this arrangement we are able to reach pressures of the order of 10^{-8} Torr in a few hours.

Attached to the bottom flange of the scattering chamber is an Ortec 3701B positioning mechanism[42]; this mechanism is provided with two arms which can be positioned independently of each other. One of the arms is used to support the electron gun. Passing through the center of rotation of the arms, a movable shaft is used to position the gas nozzle in the center of scattering. This positioning mechanism is capable of measuring the absolute scattering angle with 0.1° accuracy and 0.05° of relative error within the angular range of 0–360°. Although this accuracy can be improved[43] by one order of magnitude, we did not use this capability for our measurements.

In most previous experiments of this kind, the measurements have been restricted to large angles because scattering volumes were defined by the electron beam and by the acceptance cone of the detector. Since the scattering volume is a function of the scattering angle under these conditions, the usual procedure is to apply a simple "sine correction factor" to compensate for this effect for angles larger than 30°. Uncertainties in the scattering volume can be avoided when the scattering volume is defined by the intersection of

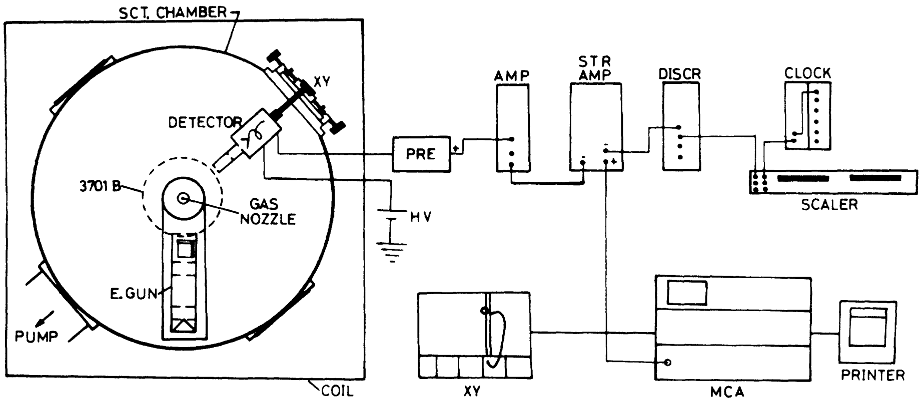

FIG. 1. Schematic representation of the apparatus utilized to measure the TDCS's.

an electron beam with the gas jet and is completely contained within the acceptance cone of the detection system. Our crossed-beam apparatus was therefore constructed to take advantage of this feature.

The electron gun[44] used is a modified version of SE-3K/5U for operation between 500 eV and 1.5 keV. This type of gun uses an Einzel lens and two pairs of deflectors which can be used to facilitate the alignment of the primary beam. The current of the primary beam is normally adjusted to 1 μA, in which case we obtain a beam of about 0.5 mm diameter measured with a phosphorescent screen. The gun is encapsulated with a tube of Pyrex and 310 stainless steel and the entire assembly is mounted in one arm of the positioning mechanism. Thus, the e gun can be rotated around the scattering center and the scattering angle read directly with the help of the proper scale.

The electron gun is operated with highly stable high-voltage power and filament supplies.[45] No fluctuation with time can be noticed in the primary beam current measured in the Faraday cup utilizing a Keithly model 602 electrometer, indicating a highly regulated beam current with fluctuation certainly below 2%.

The primary electron beam scatters from a jet of gas introduced in the system through a nozzle in the center of scattering. The nozzle is a stainless-steel tube pointed in an arrow with an internal diameter of about 0.25 mm and has an aspect ratio (length/diameter) $\simeq$100.

Before reaching the nozzle the gas from a cylinder is expanded inside an evacuated 40-liter ballast tank where the gas pressure is maintained at about 6 Torr. Prior to the injection of gas, the tank is evacuated to 10^{-2} Torr. The operation is repeated several times until we can be sure of the absence of contaminants. This was always checked with a residual-gas analyzer (Veeco[46] SPI-10) attached to the bottom flange of the vacuum chamber.

The scattered electrons were detected with a high-gain Bendix Channeltron Photomultiplier BX-7500 modified to detect electrons directly. The entrance aperture of the channeltron was positively biased in order to repel low-energy positive ions and to accelerate electrons which had suffered large energy losses owing to collisions. It is important to note that, since the detector yield is sensitive to the energy of the incoming electrons, this procedure also helps to keep the channeltron working with an approximately constant efficiency.

The acceptance angle is limited by two apertures of 200 and 300 μm placed before the detector and separated 60 mm from each other. The pulses produced by the channeltron are then preamplified, amplified, discriminated, and finally counted utilizing a SEN[42] 312–100-MHz timer-scaler. The detector and the apertures are mounted in an X-Y positioning mechanism attached to the wall of the chamber. The largest component of Earth's magnetic field in our laboratory is about 250 mG. This was compensated by use of three pairs of Helmholtz coils defining a cube with a side of one meter. The residual magnetic field in the scattering region was then kept below 10 mG.

The gas sample (research grade, 99.99% N_2) was taken directly from a cylinder furnished by White Martins.

Before the experiment, the residual pressure inside the chamber was $(3-5)\times10^{-7}$ Torr and during the experiments the gas pressure was maintained at 2×10^{-5} Torr.

The most common sources of experimental errors are the following: fluctuation of the primary electron beam current, pressure fluctuation, uncertainty in the scattering angle, scattering from the delocalized gas, and backscattering from the gas nozzle and other parts inside the vacuum chamber.

Use of a very stable and well-regulated filament and power supplies reduced considerably the fluc-

TABLE I. Theoretical [Eq. (1)] and experimental values (this work) for total (elastic plus inelastic) differential cross section for 1-keV and 500-eV electrons scattered by N_2.

Angle (deg)	$d\sigma/d\Omega$ (Å^2/sr) 1 keV Theory	1 keV Expt.	500 eV Theory	500 eV Expt.
2	82.39	78.5	···	···
4	27.11	30.1	···	···
6	13.70	14.7	···	···
8	7.557	7.64	···	···
10	4.260	3.77	9.101	8.45
12	2.499	2.61	5.956	···
14	1.587	1.66	3.943	···
15	···	···	···	2.84
16	1.106	1.12	2.661	···
18	0.8293	0.844	1.856	···
20	0.6456	0.626	1.352	1.27
25	0.3450	0.318	0.7429	···
30	0.1733	0.155	0.4779	0.449
35	0.0953	0.0989	0.3137	···
40	0.0649	0.0662	0.2014	0.204
45	0.0477	0.0485	0.1301	···
50	0.0334	0.0346	0.0905	0.100
55	0.0233	0.0259	0.0704	···
60	0.0178	0.0193	0.0590	0.0617
70	0.0120	0.0103	0.0414	0.0445
80	0.0078	0.0056	0.0272	···
90	0.0059	0.0038	0.0204	···

tuation of the beam current to a level certainly below 0.5% during the experiment. The flcutuation of the sample pressure was kept to a minimum (0.5%) by monitoring the voltage fluctuation in the ion gauge meter (NRC563-SK and Varian IG-10) with a precision digital voltmeter. In this manner we could observe and control fluctuations otherwise too fast to be observed with the meter normally supplied with the Varian IG-10 ionization-gauge controller used to measure the pressure inside the scattering chamber. We estimate that this procedure reduces the error to less than 1%. Although mechanical imperfections of our positioning mechanism do not contribute more than 0.05° error, we estimate our total error in the measurement of the scattering angle to be about 0.1° over the entire range of our measurements.

Although most of the above-mentioned factors appear to contribute very little to the uncertainty of the TDCS, the contribution from the delocalized gas does not seem to be so small. Part of this effect was compensated by measurement of the TDCS at the same pressure and introducing the gas sample through another nozzle located inside the vacuum chamber but far from the scattering center. This background caused by the delocalized gas was never more than 10% of the measurement, with electrons scattering from the gas jet introduced through the nozzle in the center of scattering. Although the background intensity caused by delocalized gas and parts inside the chamber varied from 2 to 10% of the TDCS at one particular angle, we estimate our total average error to be about 5%. The measured values of the TDCS for 1-keV and 500-eV electrons scattered by N_2 are shown in Table I.

III. THEORY

The independent atom model[32] (IAM) for scattering of high-energy electrons by molecules has been used for many years to interpret results obtained in gas-phase electron diffraction (GED). Throughout our calculations use was made of the IAM, and therefore the TDS $d\sigma/d\Omega$ for a homonuclear diatomic molecule is given by the following equation:

$$\frac{d\sigma}{d\Omega}=2\left[|f(\theta)|^2\left(1+\exp(-l_{ij}^2 s^2/2)\,\frac{\sin[s(r_g(0)+al^4s^2/6)]}{sr_{ij}}\right)+\frac{4}{a_0 s^4}S(s)\right]. \quad (1)$$

In Eq. (1), $a_0=0.5291$ Å, $s=(4\pi/\lambda)\sin(\theta/2)$ is the momentum transfer, l_{ij} is the amplitude of vibration,[47] and $r_{ij}=r_g(0)-al_{ij}^2\ (1.5+1.08a^2l_{ij}^2)$, where a is the anharmonicity,[47] taken as $a=1.9$ Å^{-1}. $S(s)$ is the atomic x-ray incoherent factor, and its values were taken from existing tables.[48]

$|f(\theta)|^2$ is the elastic atomic partial-wave scattering intensity where $f(\theta)$ is defined[49,50] by

$$f(\theta)=\frac{1}{2ik}\sum_l (2l+1)(e^{2i\delta_l}-1)P_l(\cos\theta). \quad (2)$$

Values of the phase shifts δ_l for 500-eV and 1-keV electrons scattered by nitrogen atoms were computed from Schrödinger's equation for the process:

$$\phi_l''(r)+[k^2+2V(r)-l(l+1)/r^2]\phi_l(r)=0. \quad (3)$$

In this equation $V(r)$ is the scattering potential and $k=2\pi/\lambda$; λ is the wavelength of the incident electrons and $V(r)$ is defined by

$$V(r)=-\frac{Z}{r}+\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d\vec{r}', \quad (4)$$

where Z is the nuclear charge of the target atom and $\rho(\vec{r})$ is the diagonal of the first-order electron-density matrix[51] defined as

$$\rho(\vec{r}) = \sum_{i=1}^{z} \int d\vec{r}_1 d\vec{r}_2 \cdots d\vec{r}_z \Psi^*(\vec{r}_1, \ldots, \vec{r}_z) \times \Psi(\vec{r}_1, \ldots, \vec{r}_z)\delta(\vec{r} - \vec{r}_i), \qquad (5)$$

and $\Psi(\vec{r}_1, \ldots, \vec{r}_z)$ is the ground-state electronic wave function for nitrogen. We employed a Hartree-Fock-Clementi[52] wave function in our calculations. Equation (3) was integrated by Noumerov's method[53,54] using a program[55] written for a Burroughs 6700/7700 computer.

For 500 eV and 1 keV we included all values of $\delta_l > 10^{-6}$ rad; at 500 eV this is satisfied for $l \simeq 40$ and $l \simeq 50$ for 1-keV electrons. Computed values for $d\sigma/d\Omega$ are also listed in Table I.

IV. DISCUSSION

Although no measurements of the TDCS can be found in the literature for the medium-energy range (1–15 keV) some absolute measurements for the differential cross sections of electrons elastically scattered (EDCS) by N_2 at 500 eV were recently reported by Bromberg.[23,26] For that reason, it is interesting to compare those results with these presented here for 500 eV. In order to do so we corrected the absolute EDCS values of Bromberg for the inelastically scattered electrons by adding to them the inelastic scattering factor[48] $S(s)$.

A comparison between our results and Bromberg's values plus this inelastic term is displayed in Fig. 2. Except for the region below 12° our results are in good agreement with Bromberg's EDCS plus the total inelastic factor $S(s)$. Two normalization factors were tried; in Fig. 2 the circles represent our results matched to those of Bromberg taking into consideration all measured points and computing one constant to give the best fit between the two experimental values; the crosses represent our points matched to Bromberg's values at 45° where we expect the exchange contribution to be a minimum. Since this assumption may not necessarily be true for elastic scattering, the comparison of experimental and theoretical data using the second normalization might

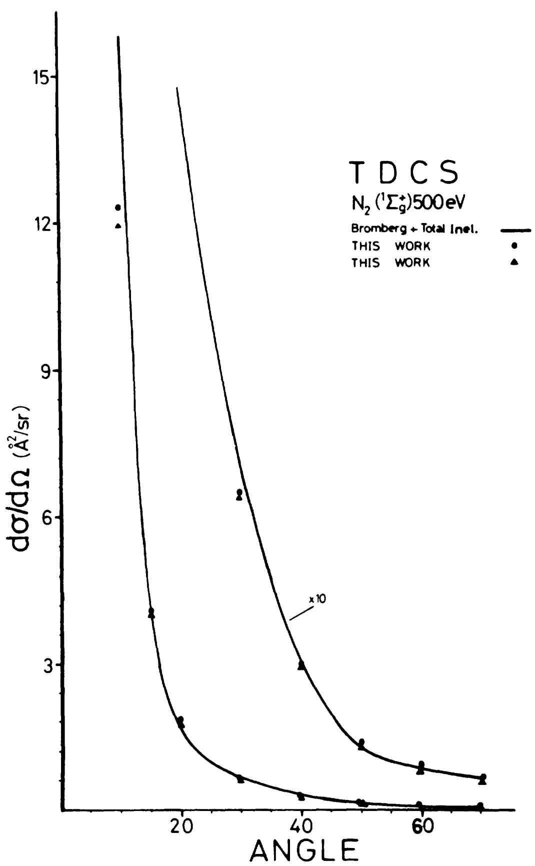

FIG. 2. Total differential cross section (TDCS) of 500-eV electrons scattered by N_2. Bromberg + total inelastic cross section (—); measured TDCS normalized to Bromberg's values at 45° (●); measured TDCS normalized to give the best fit (▲).

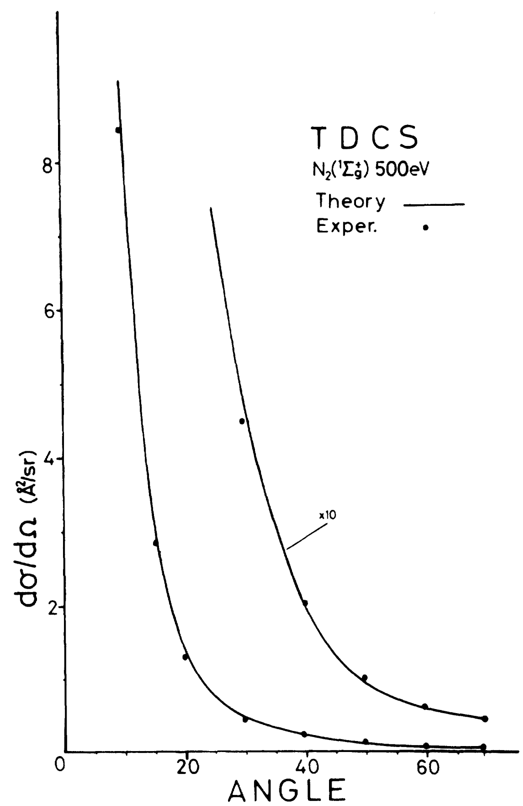

FIG. 3. Total differential cross section (elastic plus inelastic) for 500-eV electrons scattered by N_2. Theoretical values (—) were computed with Eq. (1). Experimental points of this work (●) between 6° and 80°.

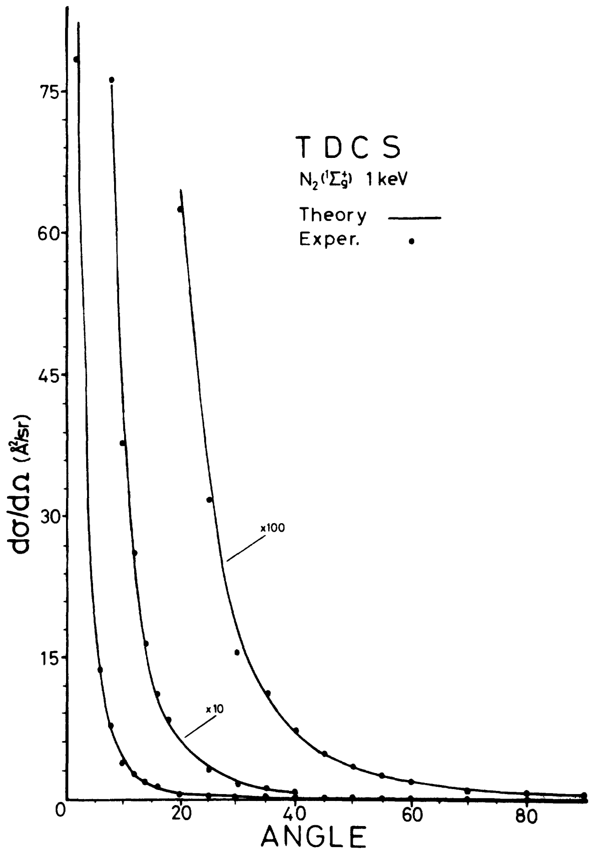

FIG. 4. Total differential cross section (elastic plus inelastic) for 1-keV electrons scattered by N_2 between 2° and 90°. Theory (—): this work, Eq. (1); experimental points measured by the authors (•).

be expected to exhibit the maximum possible deviation from the Born theory, especially in the small-angle region. However the good agreement obtained accentuates the validity of the Born approximation, even in this region.

It is also interesting to notice the agreement between the theoretical values computed with Eq. (1) and our measurements for the total differential cross section for N_2 shown in Fig. 3. From Fig. 2 and Fig. 3 we can see that the agreement between our results and theory [Eq. (1)] is better than between our results and the sum of Bromberg's values plus the inelastic scattering factor. Values of TDCS were also determined for the first time with 1-keV electron scattering from N_2. Considering the good agreement between our theoretical and experimental TDCS with 500-eV electrons, we should expect a better agreement at 1 keV. In Fig. 4 we compare our experimental and theoretical [Eq. (1)] values for 1-keV electrons and verify that the agreement between them is indeed better for 1-keV as compared to 500-eV electrons.

A good agreement between our results and the theory permits the computation of the mean amplitude of vibration l_{NN} and the internuclear distance[47] $r_g(0)$ for N_2. A least-squares fit using the data for 1 keV gave the following results: $r_g(0) = 1.096 \pm 0.005$ Å, $l_{NN} = 0.031 \pm 0.026$ Å, in very good agreement with values determined in our laboratory[56] by gas-phase electron diffraction and those previously in the literature which are cited in Ref. 56.

Good agreement between our experimental and theoretical values for 1-keV electrons proves the utility of the IAM approximation at these energies and the possibility of determining molecular-structure parameters for a large class of molecules with medium-energy electrons. Investigation of intramolecular multiple scattering is presently underway in this laboratory and initial results will soon be presented.

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