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Nitrogen total cross section for electrons below 2.0 eV*

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The total scattering cross section of molecular nitrogen for electrons in the energy range 0.3 to 1.6 eV has been measured absolutely by single-electron time-of-flight spectrometry, in which care has been taken to ensure positive removal of the scattered electrons and the gathering and reduction of data were in accordance with a thorough analysis of both statistical and systematic errors. The total cross section between 0.9 and 1.5 eV is found to be numerically equal to the momentum-transfer cross section of Englehardt, Phelps, and Risk; at lower energies it is appreciably lower than the momentum-transfer cross section. No evidence is found for the periodic structure reported in this cross section by Golden.

INTRODUCTION

Interactions of nitrogen with electrons in the energy region below the threshold for electronic excitation play a significant role in electrical conduction phenomena in the atmosphere and in gaseous electronic devices such as ionization chambers and lasers.[1] Accurate data on cross sections are essential to the design of devices and the interpretation of phenomena. This note reports measurements of the total cross section of N_2 in the energy region 0.25–2.0 eV, below the well-known 2.25-eV resonance, in which a recent compilation of cross sections[2] shows periodic fine structure which has not been satisfactorily explained.

Early determinations of the N_2 total cross section,[3-5] made before 1930, showed no low-energy structure in this cross section other than the large 2.25-eV peak. Fisk[6] explained this peak and its low-energy tail entirely on the basis of elastic potential scattering. In more recent years, Haas[7] and Schulz[8] found that inelastic processes associated with temporary formation of N_2^- also contribute appreciably (~15%) to the total cross section at the peak, although not at lower energies. Englehardt, Phelps, and Risk[9] demonstrated that measured electron transport coefficients in nitrogen can be calculated accurately if one assumes that the vibrational excitation cross section decreases from 5.5 Å^2 at 2.2 eV to less than 0.2 Å^2 at 1.7 eV and less than 0.01 Å^2 below 1.2 eV; this is consistent with calculations of excitation cross sections by Chen.[10]

In 1966, however, Golden[11] redetermined the total cross section to a claimed precision of 3%, using an improved[12] version of the Ramsauer[3] apparatus, and reported a succession of six maxima and minima between 0.4 and 1.8 eV, each amounting to nearly 25% of the total cross section. Their separations, 0.29 eV, agreed with the known interval between the lowest vibrational sublevels of the ground electronic state of N_2.[13] Similar indication of structure was reported by Boness and Hasted[14] in a transmission measurement, and Golden has recently reported observing the same resonances by a different method.[15]

Golden attributed these maxima to resonant excitation of vibrational sublevels of the $^2\Pi_g$ state of N_2^-, rather than to neutral nitrogen. This interpretation requires the minimum potential energy of N_2^- to lie no more than 0.4 eV above the $v=0$ level of N_2.[11] Other evidence places this minimum much higher: Gilmore[16] had given 1.5 eV and recent calculations of Krauss and Mies[17] give 2.5 eV for the interval between potential minima of N_2 and N_2^-.

Nakai *et al.*[18] observed changes in the time-of-flight spectra of magnetically collimated electron pulses transmitted over a long path in nitrogen, which were attributed to the temporary formation of N_2^-. They found only two values, 0.6 and 1.0 eV for the energy loss; however, since they used only a single incident energy, not all possible inelastic processes could have been excited, and their work does not bear on the validity of Golden's hypothesis.

Ehrhardt and Willmann[19] studied the angular dependence of scattering on energy losses of low-energy electrons in nitrogen, and were unable to reconcile their measurements with those of Golden. Although well-resolved vibrational fine structure was observed between 1.4 and 3.9 eV, no structure was found at lower energies. Using NO, however, a molecule isoelectronic with N_2^-, they did observe pronounced oscillatory structure in the elastic and inelastic cross sections.

The only recent absolute measurement of the total cross section of nitrogen is that of Golden; since there is reason to doubt the structure reported in this measurement, an independent determination of the absolute total cross section is desirable.

EXPERIMENTAL METHOD

The present research employed a time-of-flight (TOF) method which differs from that of all previous investigators of this problem[3-5,11,18] in the following significant respects: (i) the cross section is determined at many energies simultaneously over the entire energy range in each single run, rather than as a sequence of distinct point-by-point measurements; (ii) the electron path is long and lies entirely within the gas, and the specimen-gas pressures for comparable attenuation are correspondingly low; (iii) statistical analysis[20] provides a basis, not only for estimating the precision of the measured cross section at each energy, but also for selecting optimum experimental parameters; (iv) beam attenuations, at the optimum pressures prescribed by this analysis, are relatively much greater than in determinations for which the logarithmic derivative of transmitted current is evaluated at zero pressure[3,12]; (v) investigation of the accuracy of manometry accompanies the transmission measurements[21]; (vi) the electron energy is determined by measuring a time interval rather than a potential difference; (vii) space-charge effects are avoided, since only one electron is in transit at any time; (viii) the geometry of the present apparatus, with the drift region free of magnetic fields, ensures that scattered electrons emerge from the interaction region and are immediately collected, preventing their reaching the detector via indirect paths.

Detailed descriptions of the apparatus have been published.[22] Single electrons, generated photoelectrically by brief ultraviolet flashes focussed on a gold photoemitter, drift through 46.5 cm of gas at a sequence of measured molecular concentrations. Electrons not scattered by more than 3° are detected by a secondary-emission multiplier and registered according to their respective times of flight by multichannel analysis. The complete TOF spectrum also contains another, sharply defined group of so-called "prompt electrons" generated on a grid at the detector end of the drift tube; the position and width of this group define the effective zero TOF and the TOF resolution. Since the prompt electrons are not appreciably affected by nitrogen at the pressures employed for the transmission measurements, they provide a measure of exposure.

The total cross section is evaluated, for each TOF channel (ordinarily, each TOF channel = 12.5 nsec), by comparison of counts of electrons transmitted at various specimen-gas concentrations and normalized to equal numbers of prompt electron counts.

Nitrogen (Matheson "prepurified" grade) flowed through the spectrometer system continuously throughout each period of measurement, in order to minimize contamination by outgassing, and was removed via a well-baffled oil diffusion pump after mass analysis which verified that impurities (traces of H_2, CO, and H_2O) were not present in significant amounts. The flow rate was regulated by an Automatic Pressure Controller[23] with a Baratron[24] capacitance manometer sensor. A separate dual-head Baratron measured pressure in the scattering chamber; the deviation of its output from a preset dial value was sampled electronically and registered in the multichannel analyzer at regular intervals along with the TOF data, in order to ascertain the constancy of indicated, regulated pressure. Because of its long residence time (several minutes) in the large scattering chamber, located at a considerable distance from the exit and entrance valves, the gas was assumed to be at the temperature of the metal envelope, which was thermally insulated.

Since Baratrons are calibrated and operated with heads at 50 °C, and the apparatus was at 22 °C, corrections for thermal transpiration were applied.[21] By comparing the indications of heated and unheated heads of the dual unit over a wide range of pressures, it was found the asymptotic value of this correction, 2.6%, applied over the pressure range employed in the TOF experiments.

Each transmission run consisted of a sequence of exposure blocks, each for a preset time at a preset gas-pressure control point. Preliminary measurements demonstrated strictly exponential dependence of each channel counting rate on pressure. In one typical run, five blocks of 10 000-second exposures were registered. During the first block, the pressure was 0.5 ± 0.01 mTorr; during each of the other four blocks, 1.90 ± 0.02 mTorr; in each, the prompt electron count was within 2.5% of 24 000. In the low-pressure block, the transmitted electron counts ranged from 5000 in early TOF channels to less than 10 in late channels. The lowest energy for which a cross section was evaluated was determined in each run by the requirement that at least 100 counts had been registered; several adjacent channels were grouped together wherever necessary to meet this requirement. Occasionally the run program consisted of a sequence of three to five blocks at equally spaced pressures.

Selection of experimental parameters and computational programs for reduction of data were based on a statistical error analysis of single-electron transmission experiments by Baldwin and Miller,[20] in which it is shown that the precision of cross-section determination depends, not only on the total number of counts registered, but also on the choice of the several specimen pressures, the respective exposure times, and the precision in the reading of pressure. Data reduction was performed with an IBM-1130 computer of the RPI Linear Accelerator Laboratory.

Because of the possibility that, during the long exposures required for accumulation of statistically significant data, the TOF or pressure calibrations might drift sufficiently to destroy evidence for sharp resonances, precautions were taken to limit data accumulations to periods when perturbations of laboratory temperature were unlikely and to verify the TOF and pressure calibrations immediately at the end of each run. Nine out of a total of fifteen runs were rejected, the majority because of slight Baratron zero drifts.

RESULTS

Results of a single transmission run are compared with results of other experimenters in Fig. 1.

The TOF uncertainty, corresponding to the width of the prompt electron group, is four 12.5-nsec channels; the corresponding energy resolution at 1.5 eV (TOF = 51 channels) is 0.25 eV; at 1.0 eV, 0.13 eV; at 0.5 eV, 0.05 eV; and at 0.25 eV (TOF = 125 channels), 0.02 eV. This is adequate to resolve

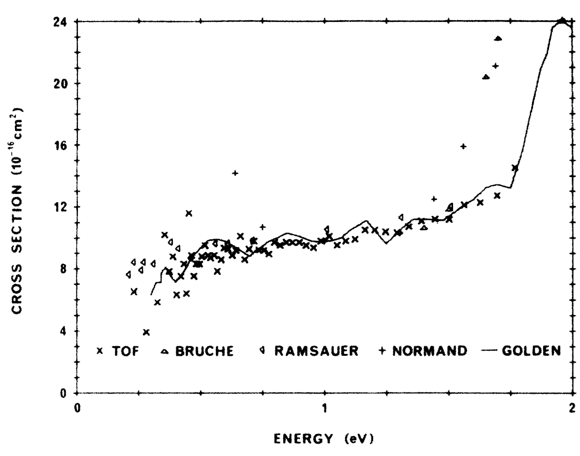

FIG. 1. Total scattering cross sections measured in nitrogen in a single TOF experiment compared with measurements by Ramsauer and Kollath (Ref. 3), Brüche (Ref. 4), Normand (Ref. 5), and Golden (Ref. 11). Each TOF data point above 0.4 eV is for a single TOF channel; channels are grouped at lower energies. Statistical rms errors, not shown, are below 6% for $0.6 < V < 1.6$ eV, increase to 10% for $V = 0.5$ eV, and to >25% for $V < 0.33$ eV; the energy resolution is given in the text.

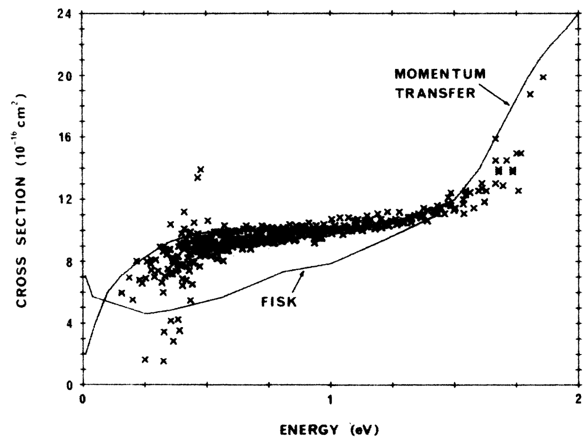

FIG. 2. All values of the total cross section measured in six separate TOF experiments in nitrogen, compared with the momentum-transfer cross section of Ref. 6. Runs of inherently lower statistical accuracy than in the run of Fig. 1 contribute to the pronounced scatter of points below 0.5 eV.

the low-energy resonances reported by Golden[11]; note that energy resolution improves as the electron energy is decreased, since TOF uncertainty is fixed.

On the other hand, at lower energies, where relatively few electrons have been emitted, statistical errors, computed from the finite numbers of registered counts and fluctuations of pressure indication,[20] are comparable with the variation in the cross section shown in Fig. 1. Thus, these variations must be attributed to statistical error and cannot be considered significant. This is demonstrated by the composite of six separate TOF runs, Fig. 2, which displays random varia-

TABLE I. Absolute total cross sections for molecular nitrogen (in Å²).

Energy (eV)	Momentum transfer[a]	Total scattering (present work)	rms absolute errors *a priori*	*a posteriori*
1.56	13.0	11.97	0.23	0.16
1.34	11.0	10.83	0.18	0.06
1.16	10.4	10.38	0.16	0.06
1.02	10.0	9.98	0.15	0.06
0.90	10.0	9.83	0.15	0.06
0.80	10.0	9.61	0.15	0.06
0.71	10.0	9.45	0.15	0.06
0.64	10.0	9.37	0.15	0.07
0.58	9.9	9.13	0.15	0.10
0.53	9.9	9.01	0.17	0.10
0.48	9.9	9.00	0.22	0.19
0.44	9.8	7.85	0.26	0.34
0.41	9.6	6.71	0.26	0.63
0.38	9.5	5.80	0.28	0.70
0.35	9.3	6.73	0.49	1.03
0.32	9.0	4.67	0.35	1.20
0.30	8.8	7.65	0.81	0.34

[a]Reference 9.

tions consistent with estimated statistical errors rather than with periodic structure.

Table I displays the weighted averages of all the determinations of the absolute total cross section in the present research. The various points of Fig. 2 have been grouped into energy bins, the widths of which correspond to the 50-nsec TOF resolution. Root-mean-square deviations have been estimated in two ways[25]: (i) *a priori*, from errors assigned to individual points according to counting statistics and pressure variation; (ii) *a posteriori*, from the deviations of individual determinations from their weighted means. Except for those low-energy bins which contain too few data for statistically significant estimation of the *a posteriori* error, it is evident that the assigned errors are conservative. There is no evidence of structure.

Between 1.0 and 1.5 eV, the present numerical values of the total cross section agree closely with the momentum cross section suggested by Englehardt *et al.*[9] At lower energy, our total cross section diminishes more rapidly than the momentum-transfer cross section.

Denoting by $I(\theta)$ the normalized probability that an electron be elastically scattered at an angle θ into the solid angle element $2\pi \sin\theta \, d\theta$, and assuming that inelastic scattering does not contribute appreciably to the total cross section, the total (Q_0) and the momentum-transfer (Q_m) cross sections are related by

$$Q_m = 2\pi Q_0 \int_0^{\pi} I(\theta)\,(1-\cos\theta)\sin\theta\, d\theta\,,$$

and their relative difference is

$$\frac{Q_m - Q_0}{Q_0} = -\tfrac{1}{4}\int_0^{2\pi} I(x/2)\sin x\, dx\,.$$

If the scattering is isotropic, $I(\theta) = \text{const.}$, or, more generally, if $I(\theta) = I(\pi - \theta)$, the two cross sections are numerically equal. Predominance of forward scattering contributes a net positive quantity to the integrand, so that then $Q_m < Q_0$; similarly, predominance of backscattering makes $Q_m > Q_0$.

According to the measurements of Ehrhardt and Willmann,[19] the scattering at 1.9 eV appears to be predominantly forward, while that at 1.4 eV may be symmetrical or even slightly backward. However, their measurements do not extend to sufficiently large angles of scattering for reliable estimates of the difference in the two cross sections. The present observations suggest that scattering between 1.4 and 1.0 eV is symmetrical, and that backscattering begins to predominate at lower energies, a trend which is consistent with the measured angular distributions.[19]

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