Near-threshold electron-impact excitation cross section for the $E\ {}^3\Sigma_g^+$ state of N_2

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The electron excitation function for the metastable states of molecular nitrogen has been analyzed to reveal the excitation cross section for the $E\ {}^3\Sigma_g^+$ metastable state of N_2. This cross section has been placed on an absolute scale by a normalization technique based on the argon metastable-atom excitation cross section. The resultant cross section is dominated near threshold by a strong, narrow negative-ion resonance. The general features of the near-threshold cross sections are entirely consistent with a number of recent excitation functions for the E state but not with previously published absolute values.

Recent analysis of transport parameters derived from electron-swarm measurements in N_2 have highlighted the uncertainty which surrounds both the shape and magnitude of the $E\ {}^3\Sigma_g^+$ excitation cross section near threshold. Tagashira, Taniguchi, and Sakai[1] and Brennan[2] have constructed Monte Carlo simulations of Townsend discharges in N_2. In both cases they found that better agreement with experiment was obtained when the cross sections of Cartwright *et al.*[3] were modified. The near-threshold behavior of these cross sections was determined by extrapolating from their lowest measured energies (15 eV) to threshold (11.874 eV), and thus they ignore the strong resonant behavior which has been observed in many high-resolution studies[4–8] which have focused on the shape and position of the resonance structure and have not attempted to assign cross sections in the threshold region. Borst, Wells, and Zipf[9] used a time-of-flight technique to study the excitation of the E state in nitrogen and determined values for the cross sections in the region near threshold.

Phelps and Pitchford[10] have compiled a complete cross section set for N_2 which is compatible with transport and excitation coefficient data. The resonant part of the E-state cross section in this compilation was derived from the data of Borst, Wells, and Zipf[9] with the energy of the peak shifted downwards by 0.3 eV in line with the more recent high-resolution studies. The discrepancy between the energy of the peak of their work (12.2 eV) and other recent work [11.90–11.95 eV (Refs. 7, 8, and 11)] can be ascribed to the poorer energy resolution, 0.6 eV, of the former. The present results are the first attempt to ascertain the near-threshold E-state excitation cross section in a high-resolution experiment.

In the present experiment, the E-state cross section has been derived from the total yield of metastable atoms as a function of incident electron energy. The incident electron beam is formed by an electron monochromator which consists of a hemispherical electrostatic energy analyzer and a series of input and output electrostatic electron lenses including a pretarget zoom lens. The monochromator is similar in some respects to that described by Brunt, King, and Read,[11] and a detailed description will not be given here. The incident electron beam is crossed at 90° with the molecular beam effusing from a 0.6-mm bore molybdenum capillary, and metastable atoms are detected by a wide-cone channel electron multiplier (CEM) (Mullard B419BL/01). The CEM is located opposite the gas-tube exit at a distance of 25 mm from the interaction region formed by the intersection of the electron and atomic beams. A suitably biased molybdenum-mesh grid, placed in front of the CEM, prevents the detection of scattered electrons. All components of the electron spectrometer are constructed from nonmagnetic stainless steel (grade 310) or molybdenum, and the system is shielded from the effects of the Earth's magnetic field by the use of Helmholtz coils and Conetic shielding. Under typical operating conditions the energy resolution [full width at half maximum (FWHM)] of the spectrometer is 20 meV and the electron beam current is about 0.5–1.0 nA.

The N_2 metastable excitation function is due primarily to contributions from the $A\ {}^3\Sigma_u^+$ ($E_{\mathrm{th}}=6.169$ eV), $a\ {}^1\Pi_g$ (8.549 eV), and $E\ {}^3\Sigma_g^+$ (11.874 eV) states.[11] The present measurement of this excitation function is in excellent agreement with the high-resolution measurement of Brunt, Read, and King[12] and, in the interest of brevity, is not reproduced here. However, the most striking feature of this excitation function is the onset just below 12 eV of the contribution from the $E\ {}^3\Sigma_g^+$ state and the subsequent series of ${}^2\Sigma_u$ and ${}^2\Pi_u$ resonances.[7] Below this threshold the excitation function is due primarily to the metastable $A\ {}^3\Sigma_u^+$ and $a\ {}^1\Pi_g$ states. In principle, the channel electron multiplier is also sensitive to ultraviolet photons in this energy range, however, the experiments of Brunt, Read, and King[12] indicate that the contribution of photons in the present work is negligible below an incident energy of 13 eV.

The near-threshold E-state excitation function was extracted from the overall metastable excitation function by fitting the smoothly varying section of the excitation function for 0.8 eV below 11.7 eV with a linear function and subtracting the extrapolated signal from the total metastable yield in the region between 11.874 and 12.7 eV. The two major assumptions made when using this procedure were firstly that the other main contributions to the observed yield in this energy range were smoothly varying (i.e., no significant resonant contributions), and secondly that the shape of the nonresonant yield below the E-state threshold gives a true indication of the yield in the energy range of consideration. The first problem has been addressed by surveying the available excitation functions in the literature. Mazeau *et al.*[13] have measured differential excitation functions for a number of vibrational levels of the $A\ ^3\Sigma_u^+$, none of which shows any evidence of strong structure in the 11.8–13 eV region. The A state can also be populated by cascade from the $B\ ^3\Pi_g$ or $C\ ^3\Pi_u$ states. Again, differential electron excitation functions for the B state[13] show no evidence of the decay of the $^2\Sigma_u$ or $^2\Pi_u$ resonances via the B state. Similar measurements for the C state[5,8] indicate that these resonances only decay very weakly via this state. As the $B \rightarrow C \rightarrow A$ cascade route is estimated to account for less than 20% of the total A-state excitation,[13] the assumption that the A-state contribution varies smoothly in the 11.8–13-eV region appears to be sound. The other main contribution to the total metastable excitation function comes from the $a\ ^1\Pi_g$ state and electron excitation functions for this state do show contributions from the $^2\Sigma_u$ and $^2\Pi_u$ resonances.[7] It is difficult to estimate the branching ratio for the $^2\Sigma_u$ into the a and E states from the work of Mazeau and co-workers[7,13] as they are not relative observations, but it would appear from the work of Borst[14] that the relative resonant contribution to the $a\ ^1\Pi_g$ state above the E-state threshold is very small.

The validity of the extrapolation procedure used for the determination of the nonresonant background in the 11.8–13.0-eV region is somewhat more difficult to establish. However, from our excitation function (and other measurements[5,9,11]) it appears that the shape of the cross section below and above the 11.8–13.5-eV resonance region is consistent with a smoothly varying nonresonant cross section throughout this region. This, together with the observation of Borst, Wells, and Zipf[9] that the near-threshold E-state cross section contains no substantive nonresonant part, gives us confidence that our fitting procedure gives a reasonable estimate of the nonresonant background in this region range.

The derived E-state excitation function is placed on an absolute scale by normalizing to the cross section for excitation of metastable argon of Buckman *et al.*[15] This was achieved by running consecutive experiments in N_2 and Ar under identical electron-optical conditions and carefully controlled gas-pressure conditions. The relative gas number densities were obtained by monitoring the background chamber pressure with an ion gauge (GP274013) and applying the manufacturer's ionization calibration factors. Care was taken to ensure that all

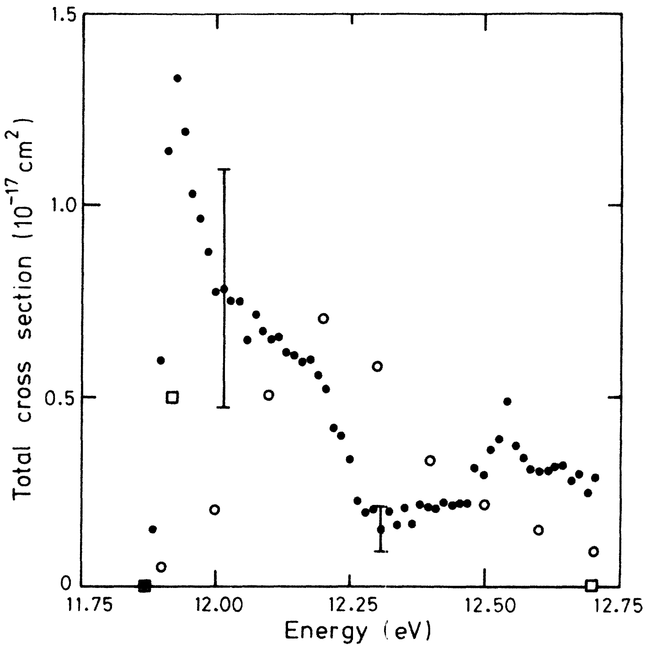

FIG. 1. Cross sections for the excitation of the $E\ ^3\Sigma_g^+$ state in the near-threshold region. The error bars represent plus and minus 1 standard deviation. ●, present results; □, Phelps and Pitchford (Ref. 10); ○, Borst *et al.* (Ref. 9).

TABLE I. Excitation cross sections for the $E\ ^3\Sigma_g^+$ state in N_2 as a function of energy.

Energy (eV)	Q (10^{-17} cm^2)
11.868	0.01
11.898	0.59
11.927	1.33
11.956	1.03
11.986	0.88
12.015	0.78
12.044	0.75
12.073	0.71
12.103	0.65
12.132	0.61
12.161	0.59
12.190	0.42
12.220	0.42
12.249	0.33
12.278	0.20
12.307	0.15
12.337	0.16
12.366	0.17
12.395	0.21
12.424	0.22
12.454	0.22
12.483	0.31
12.512	0.36
12.541	0.49
12.571	0.34
12.600	0.30
12.629	0.32
12.659	0.28
12.688	0.25

spectra were obtained under conditions of molecular flow in the source nozzle by requiring that the mean free path in the capillary was much greater than the characteristic dimension of the capillary. At a back pressure of 30 mTorr we calculate the mean free path for nitrogen and argon to be of the order of 6 and 10 mm, respectively. The internal diameter of the capillary was 0.6 mm. It was further established that the metastable signal rates were proportional to gas pressure for the range of pressures used for both gases. We have also assumed that the detection efficiencies for N_2 E metastable states and argon $3p^5 4s$ ($J=2$ and $J=0$) metastable states is the same. This assumption is based on the proximity of the thresholds of the two argon states, 11.548 and 11.723 eV, respectively, and the threshold of the E state at 11.874 eV. The cross-section normalization was carried out at a number of energies above 11.874 eV, all of which yielded consistent values. The energy scale in the present measurements was calibrated by comparing our high-resolution argon excitation functions with those of Brunt, King, and Read[16] using the feature labeled b_4 at 11.845 eV.

The derived $E\ ^3\Sigma_g^+$-state cross section is shown in Fig. 1 and tabulated values at selected energies are given in Table I. The present measurements only extend for about 1 eV above threshold, as this is the region where the resonant contributions are important and also because contributions from uv photons may become significant above 13 eV.[11] The estimated uncertainty in the present absolute measurements is 40% and arises from a statistical uncertainty ($<2\%$), gas pressure and electron-beam current fluctuations (5%), the uncertainty in the background subtraction (10%), possible energy-dependent variations due to the operation of the zoom lens (5%), and the major contribution, the normalization to the cross section of Buckman *et al.*[15] (37%). This last figure is composed of uncertainties in the cross sections of Chutjian and Cartwright[17] which were used by Buckman *et al.* to normalize their data as well as relative uncertainties in the measurements of Buckman *et al.* Also shown in Fig. 1 are the cross sections of Borst, Wells, and Zipf[9] and Phelps and Pitchford.[10]

We find that the peak in the cross section is about a factor of 2 higher than that deduced by Phelps and Pitchford.[10] This will have a significant effect not only on the cross section set used in the analysis of swarm experiments, but it also is relevant in the analysis of excitation coefficients for the $C\ ^3\Pi_u$ state. For example, Golden, Burns, and Sutcliffe[8] have attributed the population of the C state to collisional deexcitation of the E state. Clearly the cross section for the excitation of the E state is an important parameter in such studies, and the present data may explain in part why Phelps and Pitchford[10] were obliged to increase the C-state cross section by a factor of 2 to obtain agreement between calculated and measured excitation coefficients for the C state.

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