Excitation of the Metastable $E\ ^3\Sigma_g^+$ State of N_2 by Electron Impact*

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The contribution of the $N_2(E\ ^3\Sigma_g^+)$ state to the total metastable excitation function of N_2 was assessed on the basis of previous time-of-flight studies of metastable nitrogen molecules. As a result, the cross section for electron-impact excitation of the $N_2(E\ ^3\Sigma_g^+)$ state was determined in the domain of the resonance from threshold (11.87 eV) to an energy of about 13 eV. The maximum value of the cross section was found to be about 7×10^{-18} cm^2 at an energy of 12.2 eV. The measurement was made absolute by using the previously determined yield of the metastable detector, the lifetime of the E state and eliminating the energy spread in the electron beam from the primary data. The half-width (full width at half-maximum) of the resonance like excitation function near threshold was found to be about 0.4 eV. No substantial evidence was obtained from the present data for the presence of the nonresonant part of the excitation function for the $E\ ^3\Sigma_g^+$ state.

I. INTRODUCTION

Excitation of the metastable $E\ ^3\Sigma_g^+$ state of N_2 by electron impact results in a very sharp feature in the total metastable-excitation function.[1-3] In this paper the first absolute determination of the excitation cross section for the E state is presented. Relative measurements of excitation functions for this state have been previously reported.[4-6] The present measurement was made absolute by determining the efficiency of the metastable detector[7] and using the measured lifetime of the E state.[1] Because of the narrow width of the excitation function, the data had to be corrected for the energy spread in the electron beam. As a result of this study, a rather large peak cross section of 7×10^{-18} cm^2 was found for the E state near threshold, in disagreement with some earlier discussions.[3] Although the excitation function for the E state appears to consist of resonant and nonresonant parts, only the resonant part was investigated in this work because no direct evidence could be found for the nonresonant portion. Calculations appropriate for the nonresonant part show that the maximum cross section in this case should be of the order of 5×10^{-18} cm^2.[8]

II. DATA HANDLING AND RESULTS

The total metastable excitation function of N_2 obtained in previously reported time-of-flight experiments[2] using a Cu-Be-O Auger detector is shown in Fig. 1. The sharp feature in Fig. 1 near 12.2 eV was caused by metastable molecules in the $E\ ^3\Sigma_g^+$ state. In order to obtain the relative excitation function of this state, the total metastable excitation function containing the $A\ ^3\Sigma_u^+$ and $a\ ^1\Pi_g$ states but excluding the E state was interpolated and is drawn with dashed lines in Fig. 1. The interpolation shown was obtained by measuring the total metastable excitation function for different detector distances (i.e., different metastable transit times) and detector surfaces.

Figure 1 was obtained with a Cu-Be-O surface at a distance of 6.4 cm from the collision chamber. It can be seen from Fig. 2 that increasing the de-

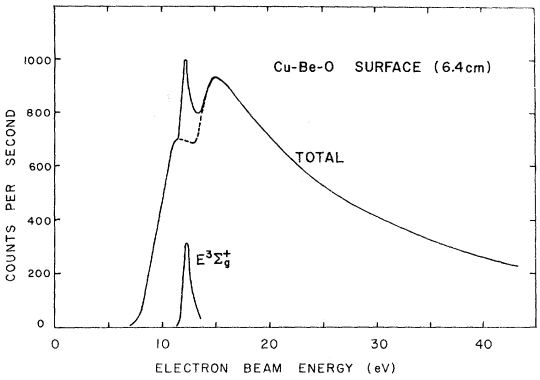

FIG. 1. Total metastable excitation function of N_2 monitored with a Cu-Be-O surface detector at a distance of 6.4 cm from the source. The sharp feature near 12 eV corresponds to excitation of the $E\ ^3\Sigma_g^+$ state. The dashed part of the total excitation function was interpolated (see text) and corresponds to metastable states other than $E\ ^3\Sigma_g^+$ (i.e., mainly $A\ ^3\Sigma_u^+$ and $a\ ^1\Pi_g$). The relative excitation function for the E state before correcting for the instrumental energy spread in the electron beam is shown near the bottom of the figure and was obtained by subtraction of the dashed from the solid curve near 12 eV.

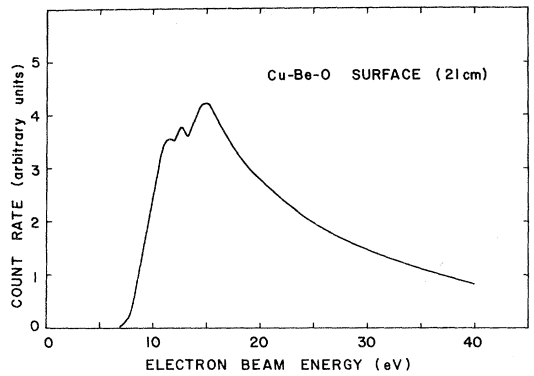

FIG. 2. Total metastable excitation function of N_2 monitored with a Cu-Be-O surface at a distance of 21 cm from the source. The contribution from the E state near 12 eV is much less pronounced than in Fig. 1 because of greater in flight metastable decay.

tector distance from 6.4 to 21 cm resulted in a marked change in the total metastable excitation function. Clearly, at larger distances the contributions from relatively short-lived metastable states such as the E state (and also the $a\,^1\Pi_g$ state) become smaller and the interpolation near 12 eV becomes rather accurate. In order to assess further the correctness of the interpolation, a tantalum surface that replaced the Cu-Be-O surface at a distance of 21 cm was used. The resulting excitation function is shown in Fig. 3. It is seen that the contribution from the E state was negligibly small although still discernible. For a tantalum surface the relative sensitivity for detecting the energetically lower lying $A\,^3\Sigma_u^+$ metastables is greatly enhanced compared to a Cu-Be-O surface, whereas the increase in sensitivity for high $E\,^3\Sigma_g^+$ metastables is not as pronounced. This makes the contribution from the E state in Fig. 3 small compared to that in Fig. 2. Based on the excitation functions in Fig. 2 and 3, we obtained the interpolation shown by dashed lines in Fig. 1 after taking into account the decrease in the $a\,^1\Pi_g$ contribution to the total metastable excitation function at the larger detector distance.

The excitation function for the E state as obtained by subtraction of the dashed from the solid curve is shown in the lower part of Fig. 1. The count rate $N(E)$ due to metastables in the $E\,^3\Sigma_g^+$ state was related to the absolute cross section $q(E)$ for this state by the expression

$$N(E)=\frac{I_b}{e}nl\,\frac{\Omega}{4\pi}\,\gamma_m C_\tau\, q(E)\,, \qquad (1)$$

where C_τ is the fraction of metastables in the E state reaching the detector, γ_m the secondary electron yield, Ω the solid angle subtended by the metastable detector at the center of the collision chamber (assuming an isotropic flux of metastables in all directions), l the effective scattering length of the collision chamber, n the absolute density of N_2 molecules in the collision chamber, I_b the beam current averaged over the period of the electron pulse, e the electronic charge, and E the electron beam energy. The cross section $q(E)$ as given in Eq. (1) is uncorrected for finite energy spread in the electron beam. Typical values for the quantities in Eq. (1) and associated errors are listed in Table I.

The scattering length l and solid angle Ω occurring in Eq. (1) were calculated from the known geometry of the collision chamber and detector configuration. The absolute gas density n was calibrated by monitoring the (0, 0) first negative band of N_2^+ at λ3914 Å for which the absolute cross section is well known.[9] The secondary electron yield γ_m for the E state was taken from the yield curve for the present Cu-Be-O Auger detector[7] at a metastable excitation energy of 11.87 eV, which corresponds to excitation of $E\,^3\Sigma_g^+$ ($v'=0$). "Franck-Condon weighting" of the yield γ_m,[2,7] which takes into account the dependence of γ_m on the vibrational levels was unnecessary for the E state, since only the $v'=0$ level appears to be strongly excited in electron impact. The details entering in the construction of the yield curve for the present detector as a function of metastable excitation energy have been previously reported.[7] It suffices to mention that the various yields obtained for different molecular and atomic metastable states followed a single smooth curve (the "yield curve"), in particular for high metastable excitation energies. From the over-all consistency in the yield curve it appears that the error in the value for γ_m listed in Table I

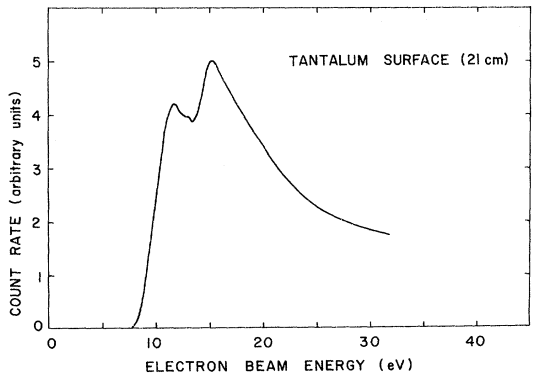

FIG. 3. Total metastable excitation function of N_2 monitored with a tantalum surface at a distance of 21 cm from the center of the collision chamber. Except for the different detector surface, the parameters were the same as for Fig. 2. (For a comparison with Figs. 1 and 2, this curve should be shifted about 0.5 eV to the left.) It is seen that the relative contribution from the $E\,^3\Sigma_g^+$ state is almost negligible.

TABLE I. Values and errors for the quantities entering in the cross section determination [see text and Eqs. (1)–(4)].

Quantity	Value	Probable error (%)
Gas density n	1.6×10^{12} cm^{-3}	20
Scattering length l	0.5 cm	15
Solid angle Ω	0.05 sr	10
Yield γ_m	0.042	20
Survival factor $C_\tau(d=6.4$ cm)	0.44	10
Beam current I_b	2×10^{-8} A	0
Deconvolution factor Γ_1/Γ_2	1.7	20
		Total error $\simeq$40% (rms)
Beam spread Γ_b	0.60 eV (FWHM)	10
Measured half-width Γ_1	0.74 eV (FWHM)	10
"True" half-width Γ_2	0.43 eV (FWHM)	20

is a realistic estimate of the uncertainty involved. Using a small center portion of the first dynode of the planar focused-mesh multiplier as the metastable detector, the collection efficiency of secondary electrons was near unity. The counting efficiency of the pulse counting system was also near unity and was determined by varying the discriminator threshold and the high voltage on the multiplier.

The fraction of metastables reaching the detector was calculated from the expression

$$C_\tau = \frac{\int_0^\infty (1/t^4)\exp(-\beta/t^2 - t/\tau)\,dt}{\int_0^\infty (1/t^4)\exp(-\beta/t^2)\,dt}\,, \tag{2}$$

where τ is the lifetime of the E state [$\tau\simeq190$ μsec (see Ref. 1)], t is the metastable transit time, and $\beta = Md^2/2kT$ is an experimentally known constant ($\beta = 2.4\times10^{-8}$ sec^2 for a detector distance $d = 6.4$ cm and room temperature). It was assumed in Eq. (2) that the time-of-flight distribution of the thermal nitrogen metastables is Maxwellian.[1] The uncertainty in the value for C_τ listed in Table I is mainly a result of the uncertainty in the lifetime τ.

Beacuse of the narrow width of the excitation function for the E state in Fig. 1, it was necessary to correct the cross section $q(E)$ in Eq. (1) for the finite energy spread in the electron beam. In order to facilitate the calculation, it was assumed that both the energy distribution in the electron beam and the measured excitation function for the E state (Fig. 1) can be approximated by Gaussian functions possessing the measured half-widths [full width at half-maximum (FWHM)] Γ_B and Γ_1, respectively. The "true" half-width of the corrected excitation function is then given by

$$\Gamma_2 = (\Gamma_1^2 - \Gamma_b^2)^{1/2}\,. \tag{3}$$

The values for Γ_1, Γ_2, and Γ_b are listed in Table I. It is seen that the corrected excitation function has a half-width of about 0.4 eV.

According to the deconvolution of Gaussian distributions, the original excitation function (Fig. 1) was scaled by a factor Γ_2/Γ_1 in width and a factor Γ_1/Γ_2 in height. This resulted in the curve shown in Fig. 4. Having determined the corrected excitation function, the absolute cross sectional scale in Fig. 4 was established from the known quantities in Eq. (1) (see also Table I). In particular, the peak cross section was obtained from the relation

$$Q_{\max} = q_{\max}\,\Gamma_1/\Gamma_2\,, \tag{4}$$

where $q_{\max}$ is the peak cross section in the original excitation function of the E state (Fig. 1). The value for $q_{\max}$ was also calculated from Eq. (1). Substituting the values from Table I into Eqs. (1) and (4), the corrected peak cross section for the E state was found to be

$$Q_{\max} = (7.0\pm4.0)\times10^{-18}\ \text{cm}^2 \tag{5}$$

at an electron energy of 12.2 eV. The probable error in Eq. (5) is an estimate based on the individual errors listed in Table I and is somewhat larger than the rms error of 40%.

The assumption of Gaussians for both the energy distribution in the beam and the original excitation function for the E state clearly represents an approximation, especially because the latter function is slightly asymmetric (Fig. 1). However, because of the existing experimental uncertainties in the shapes of the energy distribution and excitation function, it is believed that a detailed numerical deconvolution would not have resulted in greater insights.

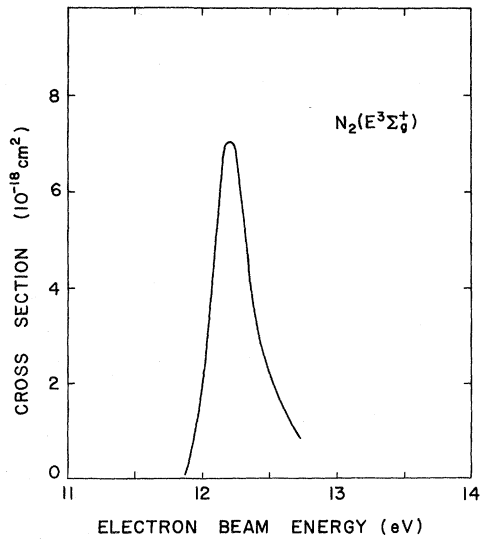

FIG. 4. Excitation cross section for the $E\,^3\Sigma_g^+$ state of N_2 as a function of electron energy. The curve shown is corrected for the finite energy spread in the electron beam (see text).

III. DISCUSSION

The narrow resonancelike shape of the present cross section (Fig. 4) is in very good agreement with a relative measurement by Ehrhardt and Willmann[5] obtained at an electron scattering angle of 20°. A direct comparison of the present curve with the relative measurement of Freund[6] is difficult because of an energy spread of more than 2 eV in the latter case.

The present peak cross section for the E state is quite large and probably larger than previously anticipated.[4] The total metastable excitation of Winters[10] contains very little contribution from the E state. While this is in contrast to the present measurements obtained with a Cu-Be-O surface (Figs. 2 and 3), it is in good qualitative agreement with the measurement obtained with the tantalum surface (Fig. 3). It seems that the nickel detector used by Winters had similar relative sensitivities for the various metastables as the present tantalum surface. Metastable transit times in Winters's work correspond to the shorter detector distance in the present work. Therefore any differences observed in the excitation functions should be mainly due to different relative detector sensitivities There also exist measurements where the E state was observed with relatively high efficiency[3] in qualitative agreement with the present observations obtained with the Cu-Be-O detector. Since none of the other measurements yielded an absolute cross section for the E state, a direct comparison is not possible.

The present method does not distinguish between neighboring vibrational levels of a high-lying metastable state such as the E state of N_2 (although this is not true for low-lying metastable states, see Ref. 2 and 7). However, it appears that the $v'=1$ level of the E state is only weakly populated (if at all) as compared to the $v'=0$ level.[11] Therefore the present result represents mainly the cross section for electron-impact excitation of $E\,^3\Sigma_g^+(v'=0)$

The excitation function reported by Heideman *et. al.*[12] for a scattering angle of 0° is much narrower than the curve in Fig. 4 and also the measurement by Ehrhardt and Willmann[5] at 20°. The present measurement integrates over all scattering angles which may result in the greater observed width of the total excitation function. Clearly, a smaller width results in a larger cross section according to the present "deconvolution" procedure. It is to be noted that the width of the curve in Fig. 4 agrees very well with that reported by Ehrhardt and Willmann.

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[1]W. L. Borst and E. C. Zipf, Phys. Rev. A 3, 979 (1971).
[2]Walter L. Borst, Phys. Rev. A 5, 648 (1972).
[3]R. Clampitt and A. S. Newton, Surface Sci. 12, 92 (1968).
[4]John Olmsted, III, Radiation Res. 31, 191 (1967).
[5]H. Ehrhardt and K. Willmann, Z. Physik 204, 462 (1967).
[6]R. S. Freund, J. Chem. Phys. 50, 3734 (1969).
[7]W. L. Borst, Rev. Sci. Instr. 42, 1543 (1971).
[8]D. C. Cartwright, Phys. Rev. A 2, 1331 (1970).
[9]W. L. Borst and E. C. Zipf, Phys. Rev. A 1, 834 (1970).
[10]H. F. Winters, J. Chem. Phys. 43, 926 (1965).
[11]A. Skerbele, M. A. Dillon, and E. N. Lassettre, J. Chem. Phys. 46, 4161 (1967).
[12]H. G. M. Heideman, C. E. Kuyatt, and G. E. Chamberlain, J. Chem. Phys. 44, 355 (1966).

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Precise High-Energy-Scattering Factors for Mercury†

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Relativistic calculations of the elastic differential cross sections for mercury at 46, 79, and 100 keV are performed using a Liberman (Hartree-Fock-Slater) potential. Various approximations for the exchange of incident and atomic electrons are considered. These calculations explain previous discrepancies between theory and experiment at higher angles.

I. INTRODUCTION

The measurement of the absolute elastic differential cross section for large-angle scattering from mercury was performed by Kessler and Weichert[1] in 1968 and has since defied satisfactory explanation