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[1]G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950).

[2]S. J. Smith, Comments At. Mol. Phys. 2, 175 (1971).

[3]R. J. Celotta, R. A. Bennett, J. L. Hall, M. W. Siegel, and J. Levine, Phys. Rev. A 6, 631 (1972).

[4]D. Spence and G. J. Schulz, Phys. Rev. A 2, 1802 (1970).

[5]M. J. W. Boness and G. J. Schulz, Phys. Rev. A 2, 2182 (1970).

[6]F. Linder and H. Schmidt, Z. Naturforsch. 26a, 1617 (1971).

[7]A. Herzenberg, J. Chem. Phys. 51, 4942 (1969).

[8]The error quoted is an estimate of error in finding the peak centers and of possible systematic error in the energy scale.

[9]Ref. 1, p. 215.

[10]M. Krauss, unpublished.

[11]Previous developmental work in this field has been reported by G. C. Baldwin and S. I. Friedman, Rev. Sci. Instrum. 38, 519 (1967); G. C. Baldwin, in *Seventh International Conference on the Physics of Electronic and Atomic Collisions. Abstracts of Papers, 1971*, edited by J. B. Hasted (North-Holland, Amsterdam, 1971), Vol. 1, p. 94; M. Y. Nakai, D. A. LaBar, J. A. Harter, and R. D. Birkhoff, Rev. Sci. Instrum. 38, 820 (1967).

[12]R. D. Hake and A. V. Phelps, Phys. Rev. 158, 70 (1967).

[13]A. V. Phelps, Rev. Mod. Phys. 40, 399 (1968).

[14]R. W. Crompton, Advan. Electron. Electron Phys. 27, 1 (1969).

[15]An uncertainty δt in the flight-time measurement produces a resolvable energy width proportional to $E^{3/2}$. Note, however, that the linewidth observed for the $v'=4$ resonance cannot be taken as a measurement of the spectrometer resolution, since the resonance has a natural width due to unresolved rotational structure (see Ref. 6).

Excitation of the $W^3\Delta_u$, $w^1\Delta_u$, $B'^3\Sigma_u^-$, and $a'^1\Sigma_u^-$ States of N_2 by Electron Impact

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Electron energy-loss spectra have been obtained for N_2 at 20.6 eV impact energy and scattering angles of 10°–138°. These spectra have been analyzed to yield the first identification of excitation to the $W^3\Delta_u$, $w^1\Delta_u$, $B'^3\Sigma_u^-$, and $a'^1\Sigma_u^-$ states in electron impact spectroscopy, and the angular dependence of the excitations from 10° to 130°. The differential cross section for excitation of the $W^3\Delta_u$ state is the largest triplet-state cross section at all scattering angles, and is the largest inelastic cross section section at angles greater than 70°.

No experimental information has yet been reported on the differential or integral cross sections for electron-impact excitation of the $W^3\Delta_u$, $w^1\Delta_u$, $B'^3\Sigma_u^-$ and $a'^1\Sigma_u^-$ states of N_2. The only available data for the excitation of these states are from calculations based on first-order perturbation models[1] for which excitation to the Σ^- states is not permitted. In this Letter we report the first observation of the direct electron-impact excitation, at 20.6 eV electron energy, of the $W^3\Delta_u$, $w^1\Delta_u$, $B'^3\Sigma_u^-$, and $a'^1\Sigma_u^-$ states, and the angular distributions for excitation of these states. The resulting cross sections differ considerably from those predicted by the first-order theories at this incident energy.

The measurements reported here were taken with a newly designed high-resolution, high-angular-range electron impact spectrometer. The spectrometer is a crossed electron-beam–molecular-beam instrument with an electron gun which can rotate from $-30°$ to $+138°$ relative to a stationary analyzer. The electron gun and ana-

lyzer were designed using tube lenses along the lines suggested by Kuyatt.[2] The electron gun utilizes a hemispherical electrostatic monochromator. The electron beam is focused onto the molecular beam, and has a calculated diameter of 0.71–0.76 mm over the incident electron energy range 3–30 eV, respectively. The divergence half-angle of the electron beam changes from 4° to 1.5° over the same range of electron energies.

The analyzer half of the electron optics consists of a second 180° electrostatic monochromator with an array of seven lenses between the scattering chamber and the second monochromator. The operating voltages for the composite lens system were determined with the aid of a computer ray-tracing program.[2] With this program, we derived all lens voltages as a function of energy lost by the electrons at constant incident energy (the "energy-loss" mode), or as a function of incident energy at a constant amount of energy lost by the electrons (the "impact-energy" mode).

The molecular beam source is a bakable stainless-steel capillary array, with a ratio of capillary length/width of 100. The electron beam crosses the molecular beam at a point about 2.54 mm above the array. Using limits defined by the angle subtended by the analyzer entrance window at the scattering center and the extreme angle of acceptance of the analyzer, we calculate the angular resolution of the instrument to be between $\pm 1°$ and $\pm 3°$. The solid angle of acceptance of the analyzer is 6.8×10^{-4} sr.

Both the gun and analyzer halves of the electron optics are bakable and are differentially pumped with respect to the main chamber. A magnetic shield reduces the residual magnetic field along the entire electron path to <5 mG. The pressure in the lens area under normal operating conditions is about 8×10^{-7} Torr when the main chamber is at 2×10^{-5} Torr. The base pressure of the main chamber is 5×10^{-8} Torr (and dropping monthly). Typical currents into a Faraday cup located near the scattering center are 1–10 nA at 8–30 eV impact energies, respectively. We have thus far taken experimental data at 8–40 eV impact energies. The spectra reported here were taken with resolutions of 0.035–0.50 eV (full width at half-maximum).

The energy-loss spectra were obtained with a 4096-channel scaler. Each energy-loss spectrum was analyzed by an iterative least-squares computer technique[3] from which we obtained the relative contribution of each electronic state to the spectrum. The technique assumes no electronic-vibrational coupling, and that the effect produced by differences in the widths of the rotational structure for different electronic states can be neglected. The validity of these assumptions and a more detailed description of the data-evaluation procedure will be published in the near future.[4] The Franck-Condon factors of the bands were calculated by the Rydberg-Klein-Rees method and numerical integration.[5] The required spectroscopic data for the B' and a' states were taken from Benesch *et al.*[6] Those for the W state were taken from Benesch and Saum,[7] and those for the w state were derived from the measurements reported by Tanaka, Ogawa, and Jursa.[8] From the computer analysis of each electron energy-loss spectrum, we obtained the relative strength of each electronic transition in the spectrum. Since the elastic intensity was also measured in the same spectrum, ratios of the intensities of the various inelastic transitions to that for the elastic scattering were also obtained at each scattering angle studied. These ratios were combined with the recent differential cross section (DCS, in arbitrary units) for elastic scattering of 20-eV electrons[9] by N_2 to obtain the relative DCS's for excitation of each electronic state present in the spectra. The normalization of these cross sections to the absolute scale was then obtained by using the integral elastic cross section[9] at 20 eV, as normalized to the absolute cross section calculations of Fisk[10] at 5 eV.

In Fig. 1 we show energy-loss spectra taken at 138° scattering angle in the energy-loss range 7.4–9.4 eV (top spectrum), and spectra taken at 115° (middle) and 20° (bottom) in the energy-loss range 9.1–11.1 eV. The upper portions of several of the strong peaks in the 20° and 115° spectra associated with bands of the $C\,^3\pi_u$ and $a\,^1\pi_g$ states have been removed for clarity. Above the spectra are vertical lines which show the locations of the vibrational bands of all the singlet and triplet electronic states in each energy-loss region. The heights of the vertical lines are proportional to the Franck-Condon factor of each band. The magnitudes of all the isolated bands in the spectra would be proportional to the heights of their lines if the electronic contributions to the DCS's were the same for *all* the electronic states. The advantage of this type of presentation is that by comparing the calculated (Franck-Condon) and actual intensities of bands of different electronic states, we can tell which electronic states are

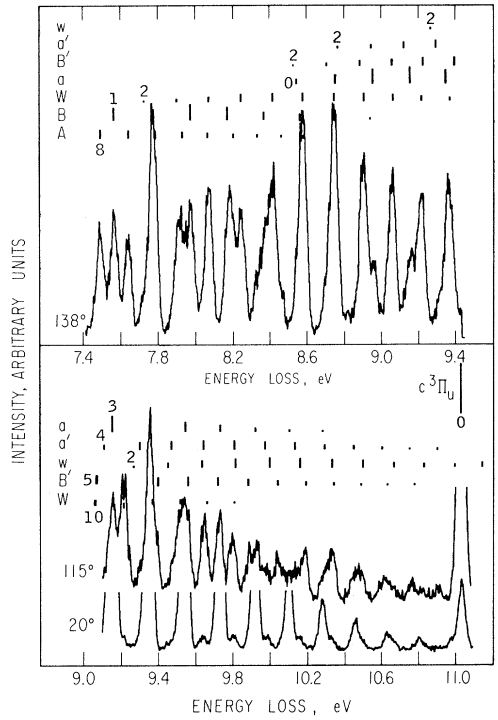

FIG. 1. Electron energy-loss spectra in N_2 at 20.6 eV incident energy and three scattering angles. The upper curve covers energy losses 7.4–9.4 eV, and the lower two curves energy losses of 9.1–11.1 eV. The vertical lines are proportional to the Franck-Condon factors for excitation to all the singlet and triplet states in these spectra. The electronic-state designations are shown to the left of the vertical lines. The numbering of the vibrational levels of each electronic state increases consecutively, starting with the left-most number.

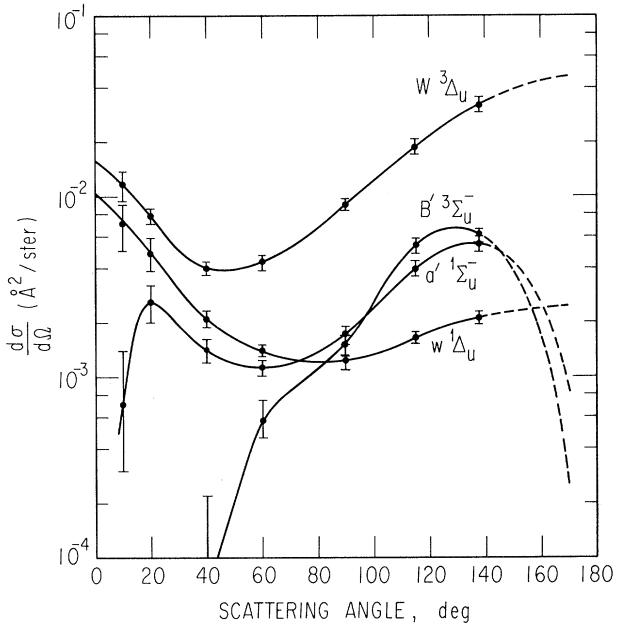

FIG. 2. Normalized differential cross sections ($Å^2$/sr) for excitation of the W, w, B', and a' states of N_2 at 20.6 eV, as determined from spectra such as shown in Fig. 1. See text for a discussion of the error limits and the dashed-line extrapolations.

important contributors to the observed peaks. For example, in Fig. 1 (138°), in addition to the strong bands of the $A^3\Sigma_u^+$ and $B\,^3\pi_g$ states, the $v'=5$ peak of the $W^3\Delta_u$ state is clearly resolved. Strong peaks corresponding to the locations of the $v'=10$ and 11 bands of the W state and $v'=5$ and 6 bands of the B' state are also present in this same spectrum. However, because the $v'=2$ and 3 bands of the B' state at lower energy losses appear only weakly, these strong peaks in the spectrum must be primarily due to bands of the W state. The substantial strength of the excitation to the W state is evident from a comparison of these strong bands with bands in the A and B states.

In Fig. 1 (20°) peaks associated with transitions to $v'=6$ and 7 of the $w\,^1\Delta_u$ state can be clearly seen. At smaller energy losses, vibrational bands of the w and a' states are nearly coincident, and could not be resolved. However, peaks due to transitions to $v'=4$ and 5 of the w state, and to $v'=7$ and 8 of the a' state, are also clearly seen between the strong bands of the $a\,^1\pi_g$ state. Figure 1 (115°) is a spectrum in which transitions to the $v'=10$, 11, and 12 levels of the B' state can be clearly seen. Many partially resolved or unresolved bands of the B', a', and w states can also be seen in this spectrum. A comparison of the spectra at 115° and 20° is particularly useful in determining qualitatively the strong dependence on scattering angle of the excitation cross sections for the various electronic states in this energy-loss region.

The DCS's for excitation by 20.6-eV electrons of the Δ and Σ^- states (obtained with the aid of our unfolding techniques[3,4]) are shown in Fig. 2. The DCS's and integral cross sections for the remaining electronic states will be presented later.[4] Smooth curves have been drawn through the data points shown in Fig. 2. The error bars indicate the 1σ confidence limits in the cross sections as determined from the unfolding analysis. The errors do not contain any estimate of the errors due to the assumptions in our unfolding procedure, or due to the normalization to the absolute scale which includes extrapolation errors in the elastic differential and integral

cross section of Shyn, Stolarski, and Carignan.[9] The confidence limit is usually large at a scattering angle for which a particular electronic state is weak and/or strongly blended. Where no error bar is shown, it is too small to be plotted. The dashed portion of each curve represents an extrapolation of the curve to 180°.

The most surprising result of the DCS's shown in Fig. 2 is the magnitude of the cross section for excitation to the $W\,^3\Delta_u$ state. As mentioned above, some indication that excitation to the W state has a relatively large cross section can be found by comparing the relative peak heights in the spectra of Fig. 1. The results of the detailed analysis[4] shown in Fig. 2 indicate that for scattering angles greater than 70°, the DCS for excitation of the W state is larger than that for excitation of any other electronic state. This DCS for excitation of the W state also leads to an integral cross section which is substantially larger than that predicted by first-order theories.[1]

The magnitudes and shapes of the DCS's for excitation of the Σ^- states are also of particular interest for two reasons. First, these are the only experimental data available on the excitation cross sections of these states for which the available theoretical results predict zero excitation cross sections.[1] From Fig. 2 we see that the cross sections for excitation of the Σ^- and $w\,^1\Delta_u$ states are comparable to one another, and only about one fifth that for excitation to the $W\,^3\Delta_u$ state. Second, it has been shown that the DCS for a $\Sigma^+ \leftrightarrow \Sigma^-$ transition produced by electron impact must vanish at 0° and 180° scattering angles.[11] The present measurements extend to small enough scattering angles to give clear indication that the DCS's for excitation of the $B'\,^3\Sigma_u^-$ and $a'\,^1\Sigma_u^-$ states do indeed follow this predicted behavior near 0°, but do not extend to large enough scattering angles to observe the predicted falloff near 180°.

It is interesting to note that the DCS of the a' state is similar to that for the B' state for scattering angles greater than about 70°, but differs considerably at smaller scattering angles. The group-theoretical considerations[11] also lead to the qualitative prediction that the DCS for a $\Sigma_g^+ \leftrightarrow \Sigma_u^-$ transition would be weaker at all scattering angles than that for a transition to an electronic state of the same orbital configuration, but of different symmetry. The B' and a' states arise from a $\pi_u{}^3\pi_g$ outer-electron configuration from which the $A\,^3\Sigma_u^+$, W, w, and $b'\,^1\Sigma_u^+$ states are also formed. The results presented here included DCS's for excitation to the Δ states and show that, except for the $w\,^1\Delta_u$ state at scattering angles greater than 70°, these qualitative expections are realized. However, the DCS's for excitation at 20.6 eV to both the B' and a' states are greater than that for excitation to the w state for scattering angles greater than about 70°. We note that the group-theoretical arguments are based entirely on symmetry properties, and therefore contain no dynamical effects which could be important at this incident energy.

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[1]D. C. Cartwright, Phys. Rev. A 2, 1331 (1970), and 5, 1974 (1972); S. Chung and C. C. Lin, Phys. Rev. A 6, 988 (1972).

[2]C. E. Kuyatt, private communication.

[3]A brief account of the computer analysis was given in S. Trajmar, D. C. Cartwright, and W. Williams, Phys. Rev. A 4, 1482 (1971).

[4]D. C. Cartwright, S. Trajmar, W. Williams, and A. Chutjian, to be published.

[5]R. N. Zare, University of California Radiation Laboratory Report No. 10925, 1963 (unpublished).

[6]W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. 142, 1227 (1965).

[7]W. M. Benesch and K. A. Saum, J. Phys. B: Proc. Phys. Soc., London 4, 732 (1971).

[8]Y. Tanaka, M. Ogawa, and A. S. Jursa, J. Chem. Phys. 40, 3690 (1964).

[9]T. W. Shyn, R. S. Stolarski, and G. R. Carignan, Phys. Rev. A 6, 1002 (1972).

[10]J. B. Fisk, Phys. Rev. 49, 167 (1936).

[11]D. C. Cartwright, S. Trajmar, W. Williams, and D. L. Huestis, Phys. Rev. Lett. 27, 704 (1971); W. A. Goddard, III, D. L. Huestis, D. C. Cartwright, and S. Trajmar, Chem. Phys. Lett. 11, 329 (1971).