Fine Structure of O_2^+ Measured by Electron Time-of-Flight Spectroscopy*

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A high-resolution electron time-of-flight spectrometer has been used in a transmission experiment to study resonances in e-O_2 scattering corresponding to vibrationally excited levels of the O_2^- $^2\Pi_g$ ground state. A doublet structure, due to spin-orbit coupling, is observed. The fine structure of O_2^- is measured to be 0.020 ± 0.002 eV, and the energy of the center of the $v' = 4$ resonance doublet is measured to be 0.091 ± 0.005 eV.

Compared with the wealth of spectroscopic data on neutral molecules and positive ions,[1] little is known about molecular negative ions, principally because of the difficulty of producing them in high densities.[2] Recently, however, measurements have been reported on the negative ion O_2^-. In a photodetachment experiment,[3] the lowest vibrational and rotational level of the $^2\Pi_g$ electronic ground state of O_2^- was measured to lie 0.440 $\pm$ 0.008 eV below the ground state of O_2. Vibrational constants of this state of O_2^- have been determined in e-O_2 scattering experiments,[4-6] in which vibrational levels with quantum numbers $v' \geq 4$ are observable as shape resonances[7] in scattering cross sections. The energy resolution of these experiments, however, was insufficient to detect structure in the resonance peaks.

In the work reported here, a high-resolution transmission experiment was performed on O_2 in an electron time-of-flight spectrometer. Resonances were observed in the total scattering cross section, corresponding to O_2^- vibrational levels with quantum numbers[5] $v' = 4$, 5, and 6 (Fig. 1). The data clearly show that each resonance peak has a doublet structure, which is due to the spin-orbit coupling in the $^2\Pi_g$ state of O_2^-. From several measurements of the $v' = 4$ resonance, the fine-structure splitting was measured to be $\Delta E = 0.020 \pm 0.002$ eV,[8] corresponding to a spin-orbit coupling constant[9] of $A = -161 \pm 16$ cm^{-1}. This agrees with a recent theoretical estimate of $A = -150 \pm 30$ cm^{-1}.[10]

An important advantage of the time-of-flight method is that the energy scale is obtained directly from the measured data. No reference is made to thresholds[6] or other energy bench marks,[4,5] which leave the energy scale uncertain by ± 0.010 eV or more. The center of the $v' = 4$ resonance was measured in this experiment to lie at 0.091 $\pm$ 0.005 eV.[8] This value, together with the O_2^- vibrational constants ($\omega_e = 0.135$ eV, $\omega_e x_e = 0.001$ eV) measured by Linder and Schmidt,[6] gives an energy for the lowest state of O_2^- which agrees well with the O_2 electron-affinity measurement of Celotta *et al.*[3]

The data of Fig. 1 are the first high-resolution results obtained by electron time-of-flight spectroscopy.[11] An electron burst 10 nsec in width is produced by sweeping a 200-eV dc beam across a narrow aperture (Fig. 2). The electrons are abruptly decelerated, and traverse a drift tube with energies in the range 0.050 to 0.400 eV. The

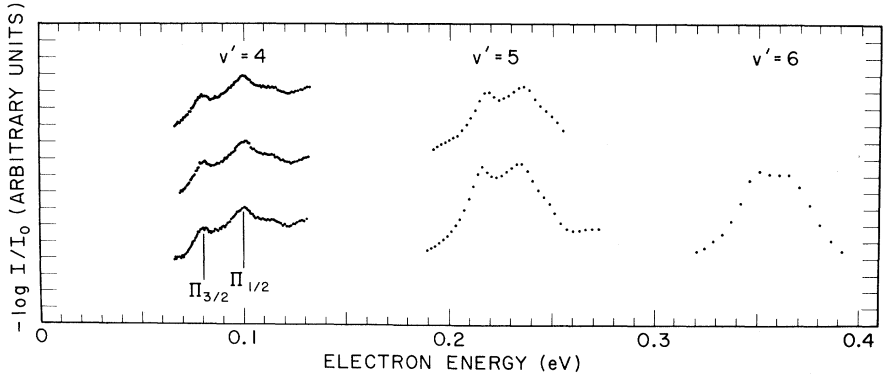

FIG. 1. Transmitted-electron scattering data for O_2. I is the count rate of electrons transmitted through the drift tube with a pressure of $\approx 10^{-2}$ Torr; I_0 is the count rate with the same gas flow by-passing the target. The statistical error, from the number of counts in each channel, lies within the dots shown.

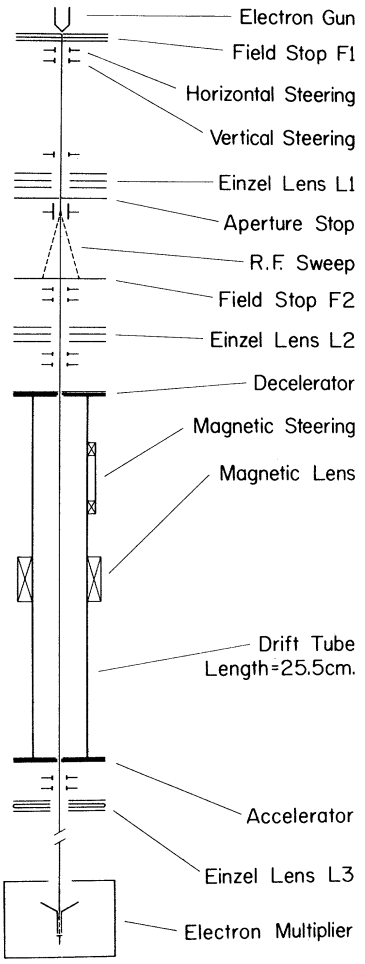

FIG. 2. Scale drawing of the electron time-of-flight spectrometer; radial dimensions enlarged by a factor of 2.

drift tube, which is 25.5 cm in length, also serves as the gas-cell target. The flight time for a single electron is determined by two time marks: the production of an electron burst, and the detection of an electron at the electron multiplier.

A time-of-flight spectrum is obtained by measuring the flight times of 10^6 or more electrons, using a time-to-amplitude converter and a multichannel analyzer. Spectra are taken (a) without gas in the target, and (b) with a gas pressure which produces a high attentuation of the transmitted electron intensity. The energy dependence of the total scattering cross section follows from a comparison of the two spectra. The spectrum taken without gas has a distribution $I_0 = f(E)$ determined by the electron-optical parameters of the system. If the spectrum taken with gas in the target, I, is related to I_0 by

$$I = I_0 e^{-NL\sigma},$$

then the negative logarithm of their ratio yields

$$-\ln(I/I_0) = NL\sigma.$$

This is the quantity plotted in Fig. 1.

The crucial question is whether other effects are present which could cause differences between I and I_0, and thus produce spurious resonance shapes. In order to minimize pressure-dependent effects at the cathode and in the electron beam outside the drift tube, the pressure in the vacuum system was held constant by feeding a constant gas flow either into the target or directly into the vacuum chamber. Changes in the contact potential of the drift tube due to the gas inlet were simulated by varying the drift-tube potential; although these tests could not rule out small changes in the slope of the cross section, no false resonances could be produced. At the target pressures used, 3 to 10 mTorr, the transmitted-electron intensity was attentuated by a factor of 100 or more in the drift tube. To obtain a sufficient counting rate, the cathode temperature was increased when taking spectra with gas in the target, but tests showed that results were independent of cathode temperature.

Prior to the work reported here, most scattering data at electron energies below 0.1 eV have been obtained from swarm experiments.[12-14] While swarm experiments can provide good absolute cross sections, they cannot reveal pronounced structure in the cross section, such as resonances. To complement the swarm data, details of narrow resonances can be provided by time-of-flight spectroscopy. It is inherent in this method that the best energy resolution is obtained at very low energies, as seen in Fig. 1.[15] Work is in progress to extend such measurements to other target gases, and to electron energies as low as 0.02 eV.

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[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-