

## Selection Rule for $\Sigma^+ \leftrightarrow \Sigma^-$ Transitions in Electron-Molecule Collisions

D. C. Cartwright

*Space Physics Laboratory, The Aerospace Corporation, Los Angeles, California 90045*

and

S. Trajmar and W. Williams

*Jet Propulsion Laboratory, Pasadena, California 91103*

and

D. L. Huestis†

*California Institute of Technology, Pasadena, California 91109*

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The differential cross section for the electron-impact excitation of the  $b^1\Sigma_g^+$  state from the ground state of  $O_2$  is found to decrease rapidly as the scattering angle approaches zero. This behavior is the diatomic-molecule analog of "parity-unfavored" transitions in electron-atom scattering. A group-theoretic argument is given which explains the observations and provides a selection rule for  $\Sigma^+ \leftrightarrow \Sigma^-$  transitions in diatomic molecules.

In a calculation of electron-impact double-excitation processes of the ground-state helium atom, Becker and Dahler<sup>1</sup> found that the differential cross section (DCS) for the transition  $1s^2^1S_g - 2p^2^3P_g$  was zero at scattering angles (relative to the incident beam direction) of  $0^\circ$  and  $180^\circ$ . This prediction has been verified experimentally<sup>2</sup> and discussed in detail by Fano for states of definite parity in terms of "parity unfavoredness."<sup>3</sup> Experimental observations of the corresponding transitions in the electron-impact excitation of diatomic molecules have not previously been reported; and, although certain selection rules determining electronic excitation within the framework of the Born approximation have been discussed previously,<sup>4</sup> no general symmetry restrictions seem to have been presented for the non-resonant<sup>5</sup> scattering of electrons by diatomic molecules. In this paper we report an observation of the analog of "parity-unfavored" transitions in atoms for the case of excitation of diatomic molecules and we present group-theoretic arguments to explain the observed behavior.

A recent study<sup>6</sup> of electron-impact excitation processes in molecular oxygen has yielded the DCS's for excitation of the  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states for incident electron energies from 4 to 45 eV and scattering in the range  $5^\circ$ - $85^\circ$ . The DCS for excitation of the  $a^1\Delta_g$  state does not possess any unusual behavior as a function of the scattering angle, but that for the  $b^1\Sigma_g^+$  state was found to decrease rapidly as the scattering angle (relative to the incident beam direction) approached  $0^\circ$ . This behavior is illustrated in Fig. 1 for an inci-

dent electron energy of 15 eV and scattering angles of  $32^\circ$ ,  $22^\circ$ ,  $12^\circ$ , and  $4^\circ$ . All four spectra have been normalized at the peak of the  $a^1\Delta_g$  ( $v' = 0$ ) level to emphasize the decrease in the  $b^1\Sigma_g^+$

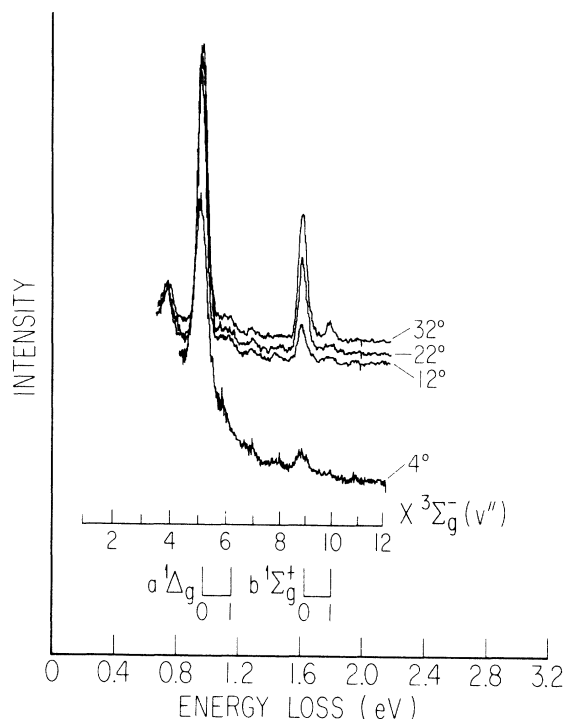


FIG. 1. Electron-impact energy-loss spectra in  $O_2$  for an incident energy of 15 eV and scattering angles of  $32^\circ$ ,  $22^\circ$ ,  $12^\circ$ , and  $4^\circ$  which show the decrease in the  $b^1\Sigma_g^+$  signal as the scattering angle is decreased. The strong background present in the  $4^\circ$  spectrum is due to contributions from the incident beam.

( $v'=0$ ) intensity. In the present apparatus, because of the finite acceptance angle and other geometrical factors, the measured signal comes from the collection of scattered electrons in a  $40^\circ$  angular region centered at the nominal scattering angle. The rapid decrease of the DCS for the  $b^1\Sigma_g^+$  excitation with decreasing scattering angle, along with direct-beam interference and errors associated with the "effective-path-length" correction,<sup>7</sup> made an accurate measurement of the small-angle behavior difficult. However, numerous additional measurements were made at small scattering angles in order to establish the symmetry of the scattered intensity around  $0^\circ$  and to minimize the uncertainty in the small-angle measurements. Figure 2 shows the resulting DCS's<sup>6</sup> for excitation of the  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states at incident energies of 10, 15, and 20 eV. Smooth curves have been drawn through the experimental data points and the error bars on the 15-eV DCS's indicate typical statistical uncertainties in the values of the DCS's. The DCS for the  $a^1\Delta_g$  state has been extrapolated smoothly from  $5^\circ$  to  $0^\circ$ .

The following group-theoretic argument shows that the DCS for electron-impact transitions of the type  $\Sigma^- \rightarrow \Sigma^+$  in diatomic molecules is zero for scattering angles of  $0^\circ$  and  $180^\circ$  at all incident

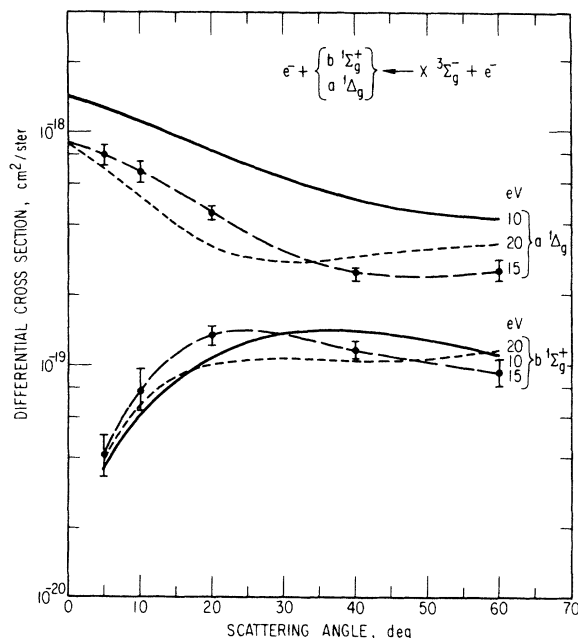


FIG. 2. Absolute differential cross sections for excitation of the  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states of  $O_2$  for incident electron energies of 10, 15, and 20 eV. The error bars on the 15-eV data points indicate the magnitude of the statistical errors present at each scattering angle.

energies. For generality in dealing with all  $\Sigma^- \rightarrow \Sigma^+$  transitions, the relevant group of symmetry operations for the electron plus diatomic molecule is taken to be  $C_{\infty v}$ . The additional information which can be obtained from the higher symmetry of homonuclear diatomic molecules ( $D_{\infty h}$ ) will be discussed below. Since the electronic portion of the total Hamiltonian for the electron plus diatomic molecule is invariant under elements of the group  $C_{\infty v}$ , the total electronic wave function ( $N+1$  electrons) in the initial and final channels must transform according to the same product representation of  $C_{\infty v}$ .<sup>8</sup> The wave function describing the incident electron,  $\varphi_i$ , can be decomposed into a sum of functions according to<sup>9</sup>

$$\varphi_i = f_+^{(1)} + f_-^{(2)} + \sum_{j=3}^{\infty} \sum_{\alpha=1}^2 f_{\alpha}^{(j)}, \quad (1)$$

where  $f_{\alpha}^{(j)}$  is a function transforming according to the  $\alpha$ th row of the  $j$ th irreducible representation of  $C_{\infty v}$ . The wave functions for the  $N+1$  electrons in the initial and final channels can be taken as simple product functions,

$$\Psi_i = \varphi_i \psi_i, \quad \Psi_f = \varphi_f \psi_f, \quad (2)$$

since the antisymmetrizing operator does not affect the other transformation properties. If we take as a specific example the excitation  $b^1\Sigma_g^+ - X^3\Sigma_g^-$  in molecular oxygen, the molecular wave functions  $\psi_i$  and  $\psi_f$  transform, respectively, according to the irreducible representations  $\Sigma^-$  and  $\Sigma^+$  of  $C_{\infty v}$ . The direct product of  $\psi_i$  with each term in Eq. (1) can be formed to determine the initial channel symmetry which, when combined with  $\psi_f$ , provides information as to the symmetry character of the scattered electron. In conducting this analysis, the coordinate system is chosen such that the incident wave vector and the molecular axis lie in the  $xz$  plane (but with otherwise general orientation). In this coordinate system, the incoming plane wave  $\varphi_i$  is independent of  $y$ ; hence  $\varphi_i$  is even under  $\sigma_v^{xz}$ , and only those components which are even under  $\sigma_v^{xz}$  appear in Eq. (1). The first term in Eq. (1) transforms as  $\sigma^+$ , which means that the initial channel symmetry ( $\Gamma_i$ ) is  $\Sigma^-$ . Since the final molecular state has the symmetry  $\Sigma^+$ , conservation of channel symmetry requires that the scattered electron wave function  $\varphi_f$  transform as  $\sigma^-$ . Such a one-electron symmetry, however, is not possible<sup>10</sup> and therefore this term cannot contribute to the  $\Sigma^+ - \Sigma^-$  excitation process. The next relevant term in Eq. (1) transforms like  $\pi_x$  which

means that  $\Gamma_i$  transforms like  $\Pi_y$ . Conservation of channel symmetry and the  $\Sigma^+$  final molecular state requires that the scattered electron wave function transforms as  $\pi_y$ . This argument can be extended indefinitely to the higher terms of Eq. (1) and shows that for a  $\Sigma^+ \rightarrow \Sigma^-$  transition, the components of the *incident* electron wave function which are even under  $\sigma_v^{xz}$  become components of the scattered electron wave function which are odd under  $\sigma_v^{xz}$ .

The essential result from this analysis is that since the  $x$  axis was taken as the incident beam direction, the scattered electron wave function which results from a  $\Sigma^+ \rightarrow \Sigma^-$  transition must have zero amplitude along the  $x$  axis. The DCS for this excitation process must therefore rigorously vanish at scattering angles of  $0^\circ$  and  $180^\circ$ . This selection rule is a consequence of the fact that for *any* molecular orientation with respect to the incident beam direction, the scattered electron wave function, which results from a  $\Sigma^+ \rightarrow \Sigma^-$  transition, must transform as odd under reflection in the symmetry plane defined by the molecular axis and the beam direction. It is noted that this selection rule for the vanishing of the DCS at  $0^\circ$  and  $180^\circ$  for  $\Sigma^+ \rightarrow \Sigma^-$  transitions does not depend on the existence of inversion symmetry and thereby differs from the analogous transitions in atoms.<sup>3</sup>

Some additional information can be obtained for *general* scattering angles and *specific* orientations of the molecular axis with respect to the plane formed by the incident and scattered electrons (the scattering plane). Since the  $xz$  reflection plane, as defined above, is a nodal plane for the scattered electron wave function in  $\Sigma^+ \rightarrow \Sigma^-$  transitions, the scattering amplitude for a  $\Sigma^+ \rightarrow \Sigma^-$  transition vanishes whenever the molecular axis is in the scattering plane. In addition, for homonuclear diatomic molecules the transition  $\Sigma^+ \rightarrow \Sigma^-$  with a change in the parity of the molecular state  $\{g \rightarrow u\}$  also has zero scattering amplitude when the molecular axis is perpendicular to the scattering plane because of the existence of the  $\sigma_h$  reflection plane in the homonuclear diatomic molecule. This implies that the DCS for a  $\Sigma^+ \rightarrow \Sigma^-$  transition with a parity change should be smaller than the corresponding transition with no parity change or the similar transition in heteronuclear diatomic molecules (assuming other factors to be the same). This expectation is based on the fact that for homonuclear diatomic molecules, the range of angles for the orientation of the internuclear axis with respect

to the scattering plane is  $0^\circ$ – $90^\circ$ , and the DCS vanishes at both the end points. It is reasonable then to expect that the DCS for such an excitation should be smaller than for the other transitions for which the DCS vanishes at only one orientation angle.

There are recent experimental results, in addition to those presented here, which support the predictions made above concerning the vanishing of the DCS at  $0^\circ$  for transitions of the type  $\Sigma^+ \rightarrow \Sigma^-$ . The energy-loss measurements in  $O_2$  by Skerbele, Dillon, and Lassette<sup>11</sup> at 45 eV and a scattering angle of  $3^\circ$  are consistent with the predicted low-angle behavior in that although the transition  $a^1\Delta_g(v'=0, 1) \rightarrow X^3\Sigma_g^-$  could be readily identified, the transition  $b^1\Sigma_g^+ \rightarrow X^3\Sigma_g^-$  was too weak to be distinguished above the background. Recent high-resolution, electron energy-loss measurements in  $N_2$  by Lassette *et al.*,<sup>12</sup> Skerbele, Dillon, and Lassette<sup>13</sup> and Williams and Doering<sup>14</sup> indicate that transitions to the  $a'^1\Sigma_u^-$  and  $B'^3\Sigma_u^-$  states from the  $X^1\Sigma_g^+$  ground state are absent at  $0^\circ$  scattering angle and are very weak, if present at all, at scattering angles out to  $20^\circ$ . Carbon monoxide has also been studied under high resolution and small scattering angles by Skerbele and Lassette<sup>15</sup> and their spectra contain no indication of excitation to the  $e^3\Sigma^-$  and  $I^1\Sigma^-$  states from the  $X^1\Sigma^+$  ground state for scattering angles as large as  $12^\circ$ . Although both  $N_2$  and CO have also recently been studied<sup>16,17</sup> to scattering angles as great as  $85^\circ$  and for incident energies as low as 10 eV, the corresponding  $\Sigma^- \rightarrow \Sigma^+$  transitions have not yet been observed. This is probably because the  $\Sigma^- \rightarrow \Sigma^+$  transitions in  $N_2$  and CO are strongly overlapped by other features in the spectrum, and their detections will therefore require higher resolution than has been used to date in addition to observation at scattering angles greater than  $25^\circ$ .

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†National Science Foundation Predoctoral Fellow, 1968–1971.

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## High-Resolution Saturation Spectroscopy of the Sodium *D* Lines with a Pulsed Tunable Dye Laser\*

T. W. Hänsch,† I. S. Shahin, and A. L. Schawlow‡  
*Department of Physics, Stanford University, Stanford, California 94305*  
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The sodium *D* resonance lines have been studied in saturated absorption with a repetitively pulsed tunable dye laser. The hyperfine splitting of the  $3^2S_{1/2}$  and  $3^2P_{1/2}$  states of  $\text{Na}^{23}$  is resolved. Measurements with a delayed probe reveal a remanent hole burning in the velocity distributions of the two ground-state levels, caused by a velocity-selective optical pumping cycle. A time-resolved observation of the collisional-velocity thermalization in the presence of Ar buffer gas is reported.

In the past the techniques of laser saturation spectroscopy<sup>1-5</sup> that eliminate Doppler broadening by spectral hole burning have essentially been restricted to either gas-laser transitions or molecular transitions in accidental coincidence. Although organic-dye lasers have been tuned to atomic resonance lines,<sup>6,7</sup> they generally did not provide the required spectral resolution and stability. The present paper reports on a study of the sodium resonance lines  $D_1$  at 5896 Å and  $D_2$  at 5890 Å in saturated absorption using a repetitively pulsed tunable dye laser with an instrumental bandwidth of 7 MHz and a pulse length of 30 nsec. The use of a pulsed laser source is made possible by a recently introduced sensitive technique of saturation spectroscopy.<sup>4,5</sup> Two light beams of equal frequency are sent in opposite directions through the resonant atomic vapor, and the change in absorption for one of the beams, the probe, caused by the other, the bleaching or saturating beam, is recorded. A

saturation signal is observed if the laser is tuned close to an atomic resonance frequency, so that both light waves interact with the same atoms, i.e., those with essentially zero axial velocity.

A simplified scheme of the experimental setup is shown in Fig. 1. The narrow-band tunable dye

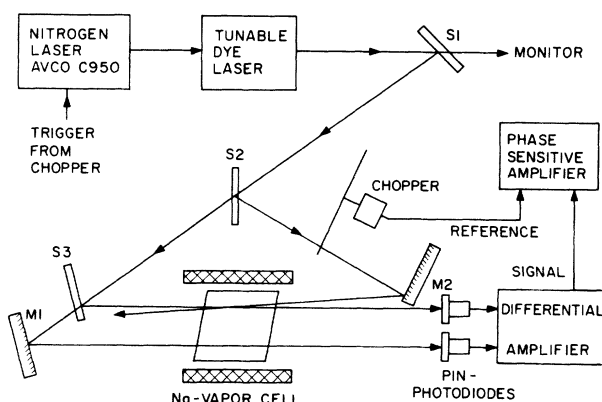


FIG. 1. Experimental setup.