

The results on the 1.27-eV affinity carbon peak, Fig. 1, are interesting because our wavelengths sample a region of rapid wavelength dependence. We still have mainly $\sin^2\theta$ behavior. However, the intercepts at 0° are larger: $14\% \pm 2\%$ at 5145 Å and $21\% \pm 2\%$ at 4880 Å. The full curves in Fig. 1 are given by Eq. (1) of Ref. 1, with the β value adjusted to give the experimental intercepts. The O^- and C^- results (deduced from the intercepts) are given in Table I.

From the good quality of the fit for O^- we can conclude that the theoretical model of Cooper and Zare (using the Robinson and Geltman potential) contains most of the physics. The wavelength variation of the C^- data is correctly predicted, but the numerical agreement and the quality of the fit are rather less satisfactory than in the oxygen case.

* This work is supported in part by the Advanced Projects Research Agency (Project DEFENDER), monitored by the U.S. Army Research Office, Durham, under Contract No. DA-31-124-ARO(D)-139.

¹ J. Copper and R. N. Zare, *J. Chem. Phys.* **48**, 942 (1968), preceding Communication.

² B. Brehm, M. A. Gusinow, and J. L. Hall, *Phys. Rev. Letters* **19**, 737 (1967).

³ M. L. Seman and L. M. Branscomb, *Phys. Rev.* **125**, 1602 (1962).

⁴ C. E. Kuyatt and J. A. Simpson, *Rev. Sci. Instr.* **38**, 103 (1967).

⁵ We are preparing a separate report of the interesting results obtained on the [62 mV] metastable negative carbon ion mentioned in Ref. 3.

⁶ L. M. Branscomb, *Atomic and Molecular Processes*, D. R. Bates, Ed. (Academic Press Inc., New York, 1962), pp. 100-140.

Differences in the Angular Dependencies of Spin- and Symmetry-Forbidden Excitation Cross Sections by Low-Energy Electron Impact Spectroscopy*

J. K. RICE† AND ARON KUPPERMANN

Gates and Crellin Laboratories of Chemistry, † California Institute of Technology, Pasadena, California

AND

SANDOR TRAJMAR

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California

(Received 30 October 1967)

Optically forbidden electronic transitions can be produced by low-energy electron impact. Recent experimental investigations of helium¹⁻³ have shown that the differential scattering cross sections for forbidden excitations are generally enhanced relative to those for allowed ones at low incident energies and large scattering angles.

We have now observed marked differences in the angular and energy dependencies of differential cross sections for various kinds of forbidden (spin, symmetry, or both) transitions in helium at low incident

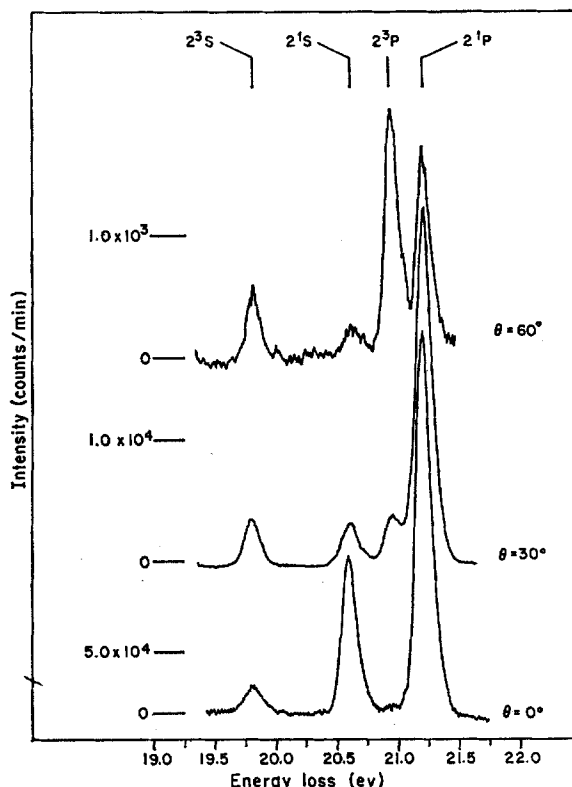


FIG. 1. Energy loss spectra of helium at 36-eV impact energy. The ordinates represent the scattered current in counts per minute. The spectra at each angle are shifted vertically as indicated by the three lines labeled 0. The three additional reference lines establish the three ordinate scales. Incident beam current: 1×10^{-8} A. Sample pressure: 6×10^{-8} torr.

energies. Such differences may well provide a basis for determining the nature of optically forbidden transitions detected by electron-impact spectroscopy in other atoms and molecules.

An electron-impact spectrometer, similar in design to those of Simpson,⁴ has been used to measure the differential cross sections for excitation from the ground state of helium to the 2^1S (symmetry-forbidden), 2^3P (spin-forbidden), and 2^3S (symmetry- and spin-forbidden) states relative to that of the 2^1P (allowed) one as a function of angle and impact energy. Double scattering events⁵ are unimportant under our experimental conditions.

Figure 1 shows representative spectra at 36-eV impact energy. Figures 2 and 3 give the intensity ratios at 36- and 46-eV impact energy, respectively. These results, together with data taken at higher (57 eV) and lower (28 eV) impact energies, support the following conclusions:

- (1) The $2^3P/2^1P$ and $2^3S/2^1P$ ratios generally increase with increasing angle, reaching broad maxima which appear to move to higher angles at lower energies.
- (2) The $2^1S/2^1P$ ratio decreases from 0° to approximately 40° and thereafter increases.

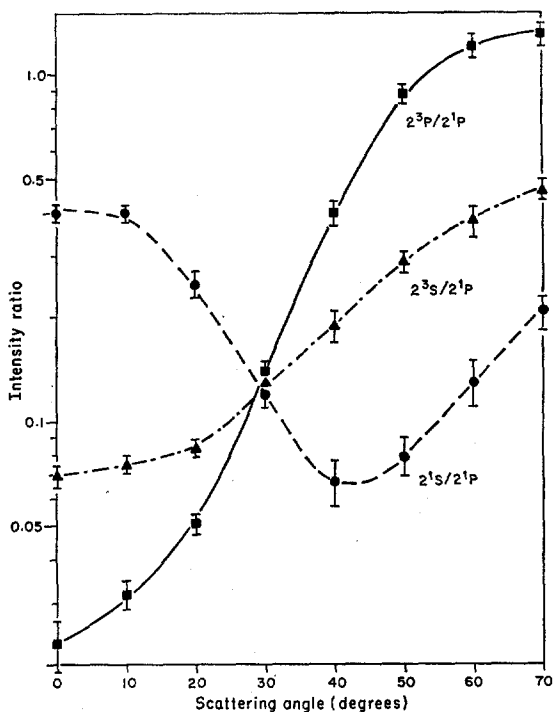


FIG. 2. Ratios of intensities of the $1^1S \rightarrow 2^3S$, 2^1S , and 2^3P transitions to that of the $1^1S \rightarrow 2^1P$ transition as a function of scattering angle. Impact energy: 36 eV. Vertical bars indicate the error limits.

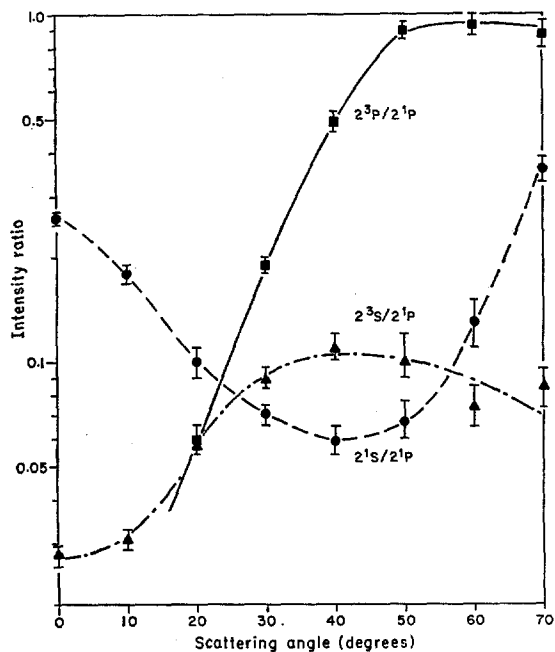


FIG. 3. Ratios of intensities of the $1^1S \rightarrow 2^3S$, 2^1S , and 2^3P transitions to that of the $1^1S \rightarrow 2^1P$ transition as a function of scattering angle. Impact energy: 46 eV. Vertical bars indicate the error limits.

(3) Lowering the impact energy does not increase the ratios at every angle. Notably, at 70° the $2^1S/2^1P$ ratio decreases from 0.5 at 57 eV to 0.2 at 36 eV.

(4) At 70° the $2^3S/2^1S$ ratio is 2.2 at 36 eV but only 0.24 at 46 eV.

The significant differences in the angular and energy dependencies of these cross-section ratios indicate the desirability of extending this investigation to other systems.

* Supported in part by the U.S. Atomic Energy Commission, Report Code No. CALT-532-16.

† Work performed in partial fulfillment of the requirements for the Ph.D. in Chemistry at the California Institute of Technology.

‡ Contribution No. 3592.

¹ G. E. Chamberlain, H. G. M. Heideman, J. A. Simpson, and C. E. Kuyatt, Proc. Intern. Conf. Phys. Electron. Atomic Collisions 4th, in *Book of Abstracts* (Science Bookcrafters, Inc., New York, 1965), pp. 378-381.

² J. A. Simpson, M. G. Menendez, and S. R. Mielczarek, Phys. Rev. **150**, 76 (1966).

³ J. P. Doering and A. J. Williams III, J. Chem. Phys. (to be published).

⁴ (a) J. A. Simpson, Rev. Sci. Instr. **35**, 1698 (1964); (b) C. E. Kuyatt and J. A. Simpson, *ibid.* **38**, 103 (1967). We thank Dr. Simpson and Dr. Kuyatt for very helpful information about the design of their instruments.

⁵ G. E. Chamberlain, J. A. Simpson, S. R. Mielczarek, and C. E. Kuyatt, J. Chem. Phys. (to be published).

EPR Observation of the Eu^{3+} to Eu^{2+} Transformation in $\text{CdF}_2:\text{Eu}^*$

M. J. VRABEL AND H. A. ATWATER

Department of Physics, The Pennsylvania State University,
University Park, Pennsylvania

(Received 9 October 1967)

We have observed the kinetics of the transformation of europium ions from trivalent to divalent charge states in $\text{CdF}_2:\text{Eu}$ under incident illumination. The europium ion enters the fluorite lattice of CdF_2 substitutionally, and may occur as Eu^{2+} or Eu^{3+} . Charge compensation in the trivalent state is normally achieved by the occurrence of an interstitial F^- ion, remote from or adjacent to the Eu^{3+} lattice site.^{1,2}

When the $\text{CdF}_2:\text{Eu}$ crystal is illuminated by mercury vapor light from which the infrared has been filtered,³ the concentration of Eu^{2+} increases typically by a factor of 2 in the as-grown crystal at low temperatures ($125^\circ\text{--}200^\circ\text{K}$). In a typical observation at 200°K the Eu^{2+} concentration increases rapidly at the start of illumination, reaching a maximum value in a time of the order of 5-10 min. The Eu^{2+} concentration thereafter falls off slowly under continued irradiation with a time constant of the order of several hours (Fig. 1).

The changes of concentration of Eu^{2+} ions were measured as a function of time after the start of illumination by observing the changes in amplitude of the