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Determination of Electronic Energy Levels of Molecules by Low-Energy Electron Impact Spectroscopy*

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THIS paper describes a new spectroscopic tool in which optically forbidden electronic transitions can usually be detected as clearly as optically allowed ones in a fairly routine manner. It uses the inelastic scattering of low-energy electrons by molecules as the means for determining their electronic energy levels.

The apparatus is a modification of that employed by Arnot and Baines.[1] Approximately monoenergetic electrons in the energy range of 25 to 100 eV are generated in a gun chamber and directed through a 1.5-mm diameter pinhole into a scattering chamber which contains a gas at about 10^{-4} mm Hg.[2] The scattered electrons are energy analyzed by a retardation-
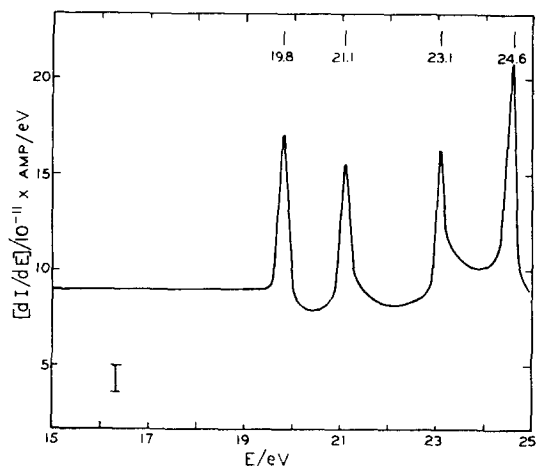

FIG. 1. Electron impact spectrum of helium. Incident electron energy: 50 eV. The vertical barred line indicates the uncertainty in the ordinate. Optical transition energies[5] from ground 1^1S state: 19.82 (2^3S), 20.61 (2^1S), 20.96 (2^3P), 21.22 (2^1P), 22.92 (3^1S). Higher energy states are so close together that they show up as a continuum in the spectrum above.
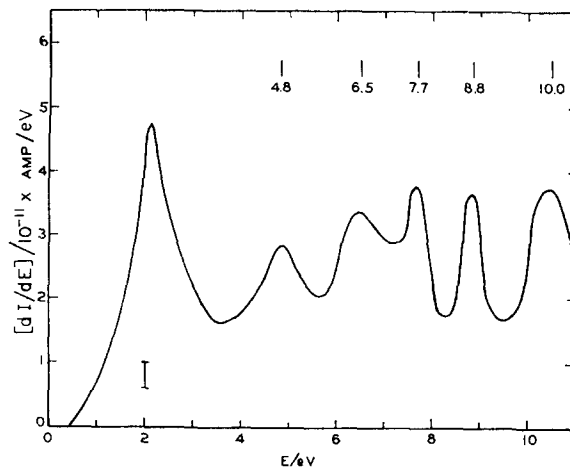

FIG. 2. Electron impact spectrum of ethylene. Incident electron energy of 50 eV.

potential method using a series of cylindrical grids coaxial with the incident beam. The current I to a cylindrical collector is measured as a function of the maximum energy loss E of the scattered electrons. The derivative, dI/dE vs E is called an electron-impact spectrum. The electronic transitions induced include optically forbidden ones, due in part to exchange scattering.[3,4] The energy scale was calibrated for each gas using its ionization peak. The correction turned out to be, on the average, only about ±0.2 eV.

The performance of the apparatus was determined using He, Ar, and H_2 as test gases. Figure 1 shows the impact spectrum of helium.[5] It can be seen that, within the inherent resolution (0.33 eV) and accuracy (±0.25 eV) of the apparatus the agreement with the optical values is excellent.

For H_2 the electron impact bands obtained are in good agreement with what would be predicted from the potential-energy diagrams for this molecule[6-8] assuming Franck–Condon transitions.[9] In particular, a band about 3.2 eV wide, with an onset at about 8.3 eV and a maximum at 9.2 eV is seen, corresponding to an excitation from the ground electronic state to the repulsive $1\ ^3\Sigma_u^+$ state.

Figure 2 shows the electron impact spectrum of ethylene at a beam energy of 50 eV. The elastic band peaking at 2 eV is shifted away from $E=0$ because of instrumental effects of a geometrical nature. The bands peaking at 7.7, 8.8, and 10.5 eV are in good agreement with the vacuum ultraviolet optical results which furnish 7.66 eV for the maximum in the $V \leftarrow N$ band,[10] onsets of 7.1, 8.2, and 8.65 eV for three $R \leftarrow N$ Rydberg series,[11] and an ionization potential of 10.45 eV.[11]

The peak at 4.8 eV agrees with the optical value of 4.6 eV obtained by Evans using the oxygen-intensification technique[12] and assigned to a vertical $T \leftarrow N$ transition of the π-electron system.[12,13] The peak at 6.5 eV is in good agreement with an optically forbidden

transition energy of 6.4 eV obtained by Potts[14] and tentatively assigned to a Rydberg triplet state.[13] Comparison of the 50-eV spectrum with ones taken at 40 and 75 eV shows that the intensity of the 4.8-eV band decreases strongly compared to the 7.7-eV band with increasing incident electron energy, as expected for spin-forbidden transitions.[4] This is in agreement with Evans' assignment. However, the intensity of the 6.5-eV band does not decrease to any significant extent in the 40- to 75-eV range of incident-electron energies, suggesting that although optically forbidden, it does not correspond to a singlet–triplet transition.[4]

Further experimental details and results will be described in a forthcoming publication.

We wish to thank Professor R. G. Parr for many stimulating discussions on this work.

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Comments and Errata

Erratum: Absorption and Fluorescence Spectra of Pr^{3+} in $LaBr_3$

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BECAUSE of a numerical error in the calculation an erroneous conclusion was drawn. On p. 1892 the statement that the 0.5% change in Slater integrals corresponds to a 0.7% increase in amount of mixing should read corresponds to a 0.3% increase in amount of mixing. The statement that the change in ζ, which goes as $\sin^2\theta$, should then result in a change of 55 cm^{-1} between $^3P_2$ and $^3P_1$ should read: corresponds to a change of 3.5 cm^{-1}, which is the order of magnitude of the actual change.

Then let ζ vary in the calculation with the restriction that ζ vary as the $(F_2)^{\frac{1}{2}}$ (since $\zeta \propto \sin^2\theta$ and $F_2 \propto \sin^4\theta$) thereby introducing no new parameters. The resulting change calculated is a 0.36% decrease in Slater integrals in going from the trichloride to the tribromide. Using this value for the change in F_2 accounts for the shift with an average deviation of 12.5 cm^{-1}, essentially the same as obtained previously. This change corresponds to 0.2% more mixing in the tribromide host than in the trichloride.

Structure of Sulfur Tetrafluoride and Related Molecules

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THE structure of sulfur tetrafluoride has recently been determined by Tolles and Gwinn from its microwave spectrum.[1] The shape of the molecule is approximately described by the statement that the fluorine atoms occupy four of the five corners of a trigonal bipyramid surrounding the sulfur, the fifth position being occupied by the lone pair of electrons. The equatorial bonds (1.545 Å) are shorter than the axial bonds (1.646 Å) and the angle between the equatorial bonds is 101°33′ while the angle between the axial bonds is 186°56′. The authors state that the structure of the molecule appears to be intermediate between that formed by using four of a set of five nonequivalent trigonal bipyramidal $sp^3d_{z^2}$ hybrid orbitals and the structure formed by using only the three p orbitals to form four bonds. This latter extreme may be described as $p^2(\frac{1}{2}p)^2$ bonding for sulfur. Although this is a reasonably satisfactory, although approximate, description of the nature of bonding orbitals involved, which is consistent with the molecular shape, it does not provide any explanation of why the molecule has a trigonal bipyramid shape, i.e., why the d_{z^2} orbital is chosen to form the set of hybrid orbitals in preference to another orbital, for example the $d_{x^2-y^2}$ orbital which gives a square pyramidal rather than a trigonal bipyramidal set of hybrid orbitals. Moreover this description of the bonding does not explain why the lone pair occupies an equatorial rather than an axial position, or why the angle between the axial bonds deviates from 180°.