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The excited states of ethylene

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In a short paper of the above title¹ I made some new assignments but left some ambiguities. One of the chief difficulties was an assignment to the "*R&L* state". However, I failed to note that the existence of this state is dubious,² and it is probably safe to ignore it. Let us do so. On the other hand, two additional well-established states now demand assignment.

Now demanding new attention are Wilkinson's optically observed *3R'* state³ and the two states just mentioned. The assignments I gave previously for higher energy states still stand. In a persuasive theoretical calculation on the singlet Rydberg states of ethylene, McMurchie, and Davidson (MD)⁴ agree with my assignments for these. However, although the assignments seem the most probable, one should admit the possibility that some of them may be wrong.

Of the two additional states, one is the upper level of the magnetic circular dichroism (MCD) spectrum found by Brith-Lindner and Allen (BLA), showing maxima at 7.2, 7.4, and 7.55 eV.⁵ The other corresponds to a peak found by van Veen (VV) in his threshold electron-impact spectrum.⁶ BLA give strong reasons for assigning the MCD state to the MO transition $\pi \rightarrow 3p\sigma$, $^1B_{2g}$ (see Table I), but admit the possibility that it might be a $\pi \rightarrow 3p\pi_y$, $^1B_{1g}$. Both give rise to an MCD spectrum, however, if and only if the transition is vibronic or non-vertical. On the other hand, MD doubted strongly that either of the two transitions could be so low in energy. The alternative would seem to be that the MCD state is a triplet state but the observed transition is much too

strong for such an assignment. The most probable answer seems to be to accept BLA's $^1B_{2g}$ assignment.

This leaves $^1B_{1g}$ as a favored candidate for the VV state. Why not $\pi \rightarrow 3p\pi_x$, 1A_g ? MD have assigned the *3R'* state to this, arguing that the experimental *3R'* is closest to their calculated 1A_g , as compared with $^1B_{1g}$ and $^1B_{2g}$; however, they do not decide conclusively among these possibilities. But $^1B_{2g}$ is now probably pre-empted. Although in planar ethylene transitions to all are forbidden for electric-dipole radiation, each of the three transitions could be made allowed by suitable vibronic interaction, borrowing strength from the VN transition.⁴ Further, all Rydberg states, like the observed $2R$ $^1B_{3u}$ state which is known to be twisted $25 \pm 1^\circ$ at equilibrium,⁷ should (like the ion) be twisted at equilibrium. This fact makes electronic-dipole transitions to them allowed, even if weakly, by nonvertical transitions, but with an energy displacement of only about 0.01 eV. A further small argument for the assignment of *3R'* to 1A_g is the precursor rule¹ in connection with the fact that according to MD's calculations this state has the highest energy of the three under consideration.⁸ [The precursors $2b_{1u}$, $1b_{2u}$, and $1b_{3u}(\pi)$ for $3p\sigma(3b_{1u})$ of $^1B_{2g}$, $3p\pi_y(2b_{2u})$ of $^1B_{1g}$, and $3p\pi_x(2b_{3u})$ of 1A_g , have respective ionization energies 18.87, 15.88, and 10.51 eV.] Note also that the precursor rule, which while only plausible and not expected to be exact,⁸ supports the choice of $^1B_{2g}$ as relatively low in energy.

If the VV state is $^1B_{1g}$, transition to it could be made allowed by the twisting (A_u) vibration ν_4 , with ν_4 about

TABLE I. Low excited states.

State	Types	Twist	Excited MO(0°)	State (0°)	Excitation energy (eV)		
					Experiment	Theory MD	Theory BP
V	semi-Rydberg	90°	$1b_{2g}(2p\pi-2p\pi, 3d\pi)$	$^1B_{1u}$	5.5 (90°) 7.65(peak)	7.96	6.22 (90°) 7.95 ^e
BLA ^a	Rydberg	~25°	$^3B_{1u}(3p\sigma)$	$^1B_{2g}$	7.2	8.01	7.7 ^h
<i>2R</i> ^b	Rydberg	25°	$4a_g(3s)$	$^1B_{3u}$	7.10	7.26	7.0 ^f
VV ^c	Rydberg	~25°	$2b_{2u}(3p\pi_y)$	$^1B_{1g}$	7.83	7.93	7.6 ^f
<i>3R'</i>	Rydberg	~25°	$2b_{3u}(3p\pi_x)$	1A_g	8.26	8.36	

^aReference 5.

^bReference 7.

^cReference 6.

^dReference 3.

^eExcept for the V state, the experimental values are presumably vertical or nearly so. Except for the V state at 90°, the theoretical values are all vertical.

^fReference 10.

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^hU. Fischbach, R. J. Buenker, and S. D. Peyerimhoff, Chem. Phys. 5, 265 (1974).

210 cm^{-1} as in the $2R-N$ transition.⁷ But it is apparently not necessary to invoke a vibronic transition, since we are told that electric dipole selection rules do not obtain to a significant degree for threshold electron-impact spectra. Further support for this assignment comes from studies on several substituted ethylenes, where intense CD peaks⁹ at energies above that of the $V-N$ transition have been assigned to the analogues of the ethylene $^1B_{1g}-N$ transition.

The most probable assignments arrived at by the foregoing considerations for the lower excited states of ethylene are summarized in Table I. Those for the higher Rydberg states are summarized in Table I of the earlier paper.

MD mention that their calculated energies are expected to be somewhat high. They note that those of a 1975 paper of Buenker and Peyerimhoff¹⁰ are about 0.3 eV lower. In their paper, MD gave a critical review of previous work on the Rydberg singlet states.

I am greatly indebted to Dr. W. M. Flicker, who has investigated the electron-impact spectrum of ethylene,¹¹ for extremely helpful correspondence, including calling my attention to Refs. 2, 5, and 6. I am also much indebted to Professor O. Schnepp and Dr. S. D. Allen for valuable discussion.

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EPR spectrum of Sb^{4+} in a silicate glass

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During the development and characterization of polychromatic glasses¹⁻³ (i. e., glasses that develop a variety of colors, depending on UV exposure and heat treatment) we observed the EPR spectrum shown in Fig. 1. It was formed by exposing a sample of this glass, which contains both Ce^{3+} and Ce^{4+} , to long wavelength UV light. It is well known⁴⁻⁶ that Ce^{3+} can be photoionized and that the released electron can be captured by intrinsic defects or by an ion of a polyvalent element.

In order to identify the EPR center it was necessary to simplify the composition of the glass systematically. The spectrum of Fig. 1 was generated in a glass of the composition $0.82 \text{ SiO}_2-0.18 \text{ Me}_2\text{O}-0.00020 \text{ CeO}_2-0.00044 \text{ Sb}_2\text{O}_3$ (Me can be K or Na). Both Ce and Sb were found to be necessary constituents.

Replacing Sb by other elements, such as Nb or Mo, which normally occur as Nb^{5+} ,^{7,8} and Mo^{6+} ,⁹ in glasses, gave rise to intense spectra of Nb^{4+} ,^{7,8} and Mo^{5+} ,^{10,11}

TABLE I. Spin Hamiltonian parameters.

	H_0	A	B
Mean	3530.8	510.6	274.6
Std. Dev.	56.5	37.4	29.4

TABLE II. Values of $|\psi(o)|^2$ for several 5s atoms and ions.

Species	Host lattice	$ \psi(o) ^2$ (cm^{-3})	Ref.
^{107,109} Ag ⁰	Phosphate glass	6.4×10^{25}	16
^{111,113} Cd ⁺	KCl	8.8×10^{25}	17
^{117,119} Sn ³⁺	CdS, CdSe	5.8×10^{25}	18