

# Vibronic structure of the second triplet state of 1,3,5-hexatriene<sup>a)</sup>

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We have used the technique of low-energy, variable-angle, electron-impact spectroscopy<sup>1,2</sup> to reinvestigate the second triplet state in a mixture of *cis*- and *trans*-1,3,5-hexatriene. This state ( $1^3A_g$  in the *trans*- and  $1^3A_1$  in the *cis*-isomer) was previously investigated by electron-impact techniques,<sup>3,4</sup> but with insufficient resolution to observe the vibrational structure reported in the present paper.

The experimental apparatus used in this study has been described previously.<sup>1</sup> Spectra of 1,3,5-hexatriene in the 3.5–6.0 eV energy-loss range were obtained at 50 eV incident electron energy over scattering angles from 5° to 80°. The 1,3,5-hexatriene sample was obtained from the Aldrich Chemical Company with a stated chemical purity of 99%. The sample was a mixture of the *cis*- and *trans*-isomers. Gavin *et al.*<sup>5</sup> reported that their Aldrich sample was 60% *trans*-isomer, while Post *et al.*<sup>6</sup> found their Aldrich sample to contain about 90% *trans*-isomer. The isomeric shifts in the optical spectra between the  $1^1B_u$  (*cis*) and the  $1^1B_2$  (*trans*) states (which occur at about 4.9 eV excitation energy) was approximately 0.016 eV,<sup>5</sup> which is significantly less than our resolution (see Fig. 1). For this reason we did not perform an isomer analysis of our sample. For ease of reference, the symmetry of the *trans*-isomer will be used in the designations of the present study.

Figure 1 shows the spectrum of 1,3,5-hexatriene at scattering angles of 5°, 40°, and 60°. As is expected for a singlet–triplet transition,<sup>1,2</sup> the  $\tilde{X}^1A_g \rightarrow 1^3A_g$  excitation, occurring in the range of 3.6–4.5 eV becomes more intense with respect to the  $\tilde{X}^1A_g \rightarrow 1^1B_u$  transition, exhibited between 4.6 and 6.0 eV, as the scattering angle increases. Four vibronic peaks are reproducibly observed at 3.75 ( $\pm 0.01$ ), 3.92 ( $\pm 0.01$ ), 4.07 ( $\pm 0.02$ ), and 4.20 ( $\pm 0.02$ ) eV.

In order to assign these bands, it is necessary to know the symmetry selection rules that govern the corresponding electron impact singlet–triplet transitions. Cartwright, Kuppermann, and co-workers<sup>7–9</sup> found that at 50 eV incident electron energies the Ochkur–Rudge approximation<sup>10</sup> yielded integral and differential cross sections for atomic and molecular hydrogen in good agreement with available experimental results.<sup>8,9</sup> Within the framework of this approximation the main contribution to the transition intensities comes from the electric dipole term and, to a lesser extent, from higher electric multipole terms. For a series of fluorinated benzenes, Frueholz *et al.*<sup>11</sup> found that optical electric dipole selection rules were somewhat, but not

entirely, relaxed in the 50 eV electron impact spectra. In light of these facts we expect the  $\tilde{X}^1A_g \rightarrow 1^3A_g$  transition in our electron impact spectra to observe vibronic<sup>12</sup> electric dipole propensity rules.

For the *trans*-isomer, transitions to  $A_g$  states will be electric dipole-forbidden,<sup>12,13</sup> and we expect the 0,0 band of the  $\tilde{X}^1A_g \rightarrow 1^3A_g$  excitation to be absent or weak. The vibronic feature occurring at 3.75 eV is significantly weaker than the other observed vibronic components. We tentatively assign it as the 0,0 band. The presence of this band may be due to the weakening of the dipole selection rules or to the presence of the *cis*-isomer for which  $A_1 \rightarrow A_1$  transitions are electric dipole-allowed. The *trans*-isomer electric dipole selection rules require the total vibronic symmetry of the excited state to be  $A_u$  or  $B_u$ . As a result, vibronic bands for  $A_g$  states result from the excitation of an odd number of  $A_u$  or  $B_u$  vibrational quanta.

The band occurring at 3.92 eV probably corresponds to the excitation of a single quantum to a vibration of  $A_u$  or  $B_u$  symmetry with an energy of about 0.17 eV (1400  $\text{cm}^{-1}$ ). The ground state vibrational spectra of both *cis*- and *trans*-1,3,5-hexatriene have been assigned by Lippincott and Kenny.<sup>14</sup> In an optical study of hexatriene, Gavin *et al.*<sup>5,15</sup> found that vibrations observed in the excited states had wavenumbers very similar to the corresponding ground state vibrations (within 60  $\text{cm}^{-1}$ ). Within our energy resolution and accuracy, the use of ground state vibrational wavenumbers is justified. The most reasonable assignment of the 3.92 eV band for the *trans*-isomer is to a vibrational state of  $B_u$  symmetry, having a single quantum of the in-plane  $\text{CH}_2$  scissor mode (1429  $\text{cm}^{-1}$ ). The corresponding transition in the ground electronic state infrared spectrum is strongly allowed. For the *cis*-isomer the infrared spectrum has an analogous strong absorption at 1449  $\text{cm}^{-1}$ .<sup>14</sup>

TABLE I. Assignment of the vibronic components of the second triplet state of 1,3,5-hexatriene.

Transition Energy (eV)	Vibrational quanta excited <sup>a</sup>
3.75 $\pm$ 0.01	0
3.92 $\pm$ 0.01	$1\nu_{sc}$
4.07 $\pm$ 0.02	$1\nu_{sc} + 1\nu_{bend}$
4.20 $\pm$ 0.02	$1\nu_{sc} + 2\nu_{bend}$

<sup>a</sup> $\nu_{sc}$  refers to the in-plane  $\text{CH}_2$  scissor mode and  $\nu_{bend}$  to the CH in-plane bending mode, Ref. 14.

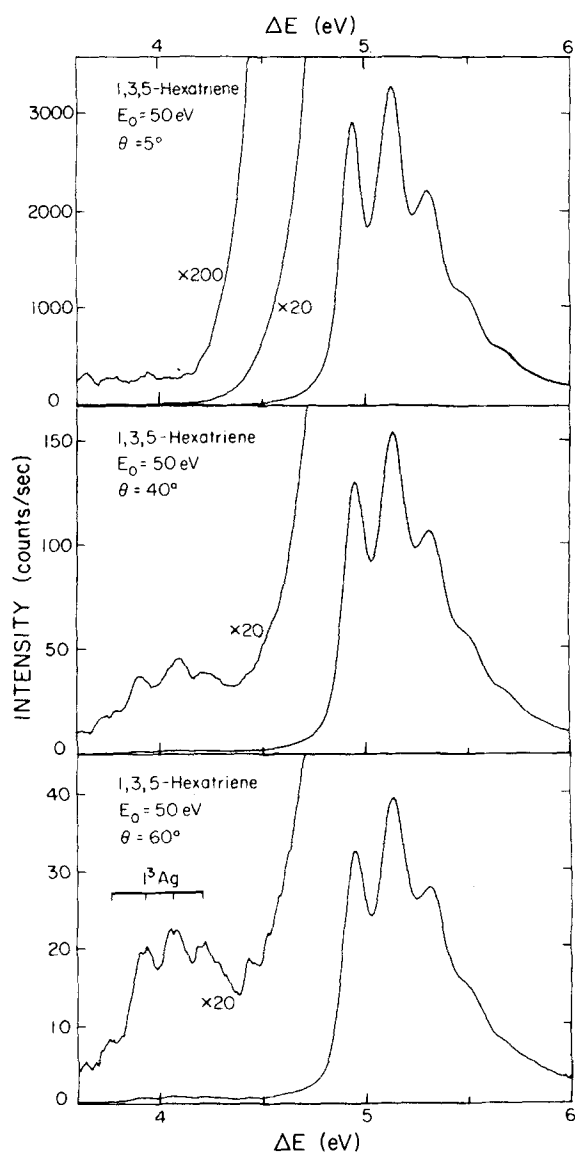


FIG. 1. Electron energy-loss spectra of 1, 3, 5-hexatriene at scattering angles of  $5^\circ$ ,  $40^\circ$ , and  $60^\circ$ ; 50 eV incident electron energy; 80 nA incident beam current; 6 mTorr sample pressure reading from an uncalibrated Schulz-Phelps gauge; resolution approximately 0.090 eV (fwhm). The apparent structure on the top of the peaks at 3.92, 4.07, 4.20 eV in the  $60^\circ$  spectrum are not reproducible and represent instrumental noise.

The spacing between the 3.92 eV band and the 4.07 eV band is  $1200\text{ cm}^{-1}$  while the spacing between the 4.07 eV band and the 4.20 eV band is  $1050\text{ cm}^{-1}$ . We attribute the latter two bands to the excitation of a single quantum of the  $\text{CH}_2$  scissor mode plus one and two quanta, re-

spectively, of an  $A_g$  vibration. The CH in-plane bending mode appears very strongly in the ground state Raman spectrum, occurring at  $1187\text{ cm}^{-1}$  for the *trans*-isomer and at  $1182\text{ cm}^{-1}$  for the *cis*-isomer.<sup>14</sup> This is analogous to the vibronic A bands of the  ${}^1B_{2u}$  electronic state of benzene.<sup>16</sup>

These assignments are summarized in Table I. We believe that they furnish a likely identification of the present newly observed vibronic structure of the spin-forbidden  $\bar{X}{}^1A_g - 1{}^3A_g$  transition in 1, 3, 5-hexatriene.

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