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# Electron impact excitation of the $\tilde{a}^3B_{1u}$ electronic state in $C_2H_4$ : An experimentally benchmarked system?

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We report on differential and integral cross section measurements for the electron impact excitation of the lowest-lying triplet electronic state ( $\tilde{a}^3B_{1u}$ ) in ethylene ( $C_2H_4$ ). The energy range of the present experiments was 9 eV–50 eV, with the angular range of the differential cross section measurements being  $15^\circ$ – $90^\circ$ . As the ground electronic state of  $C_2H_4$  is a  $^1A_g$  state, this singlet  $\rightarrow$  triplet excitation process is expected to be dominated by exchange scattering. The present angular distributions are found to support that assertion. Comparison, where possible, with previous experimental results from the University of Fribourg group shows very good agreement, to within the uncertainties on the measured cross sections. Agreement with the available theories, however, is generally marginal with the theories typically overestimating the magnitude of the differential cross sections. Notwithstanding that, the shapes of the theoretical angular distributions were in fact found to be in good accord with the corresponding experimental results. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4716184>]

## I. INTRODUCTION

A knowledge of absolute differential and integral cross sections for electronic-state excitation of small polyatomic molecules is fundamental for an improved understanding and modelling of the low-pressure discharge plasmas employed in many industries. In particular, ethylene ( $C_2H_4$ ) is employed as a feed-stock gas in plasma polymerisation processes.<sup>1</sup> Those cross sections are also potentially a valuable further source of information on transient anions (resonances) and their decay dynamics. The interest in these cross sections has been promoted by continuing advances in the capabilities of high-performance computers and with the development of theoretical methods for electron-molecule scattering, making it possible to attempt detailed *ab initio* studies of electronic-state cross sections for even large polyatomic molecules. Ethylene, in this respect, represents an ideal prototype system as its “chromophore”, responsible for resonance phenomena at low energies, is a C=C double bond with  $\pi$  and  $\pi^*$  orbitals typical of unsaturated organic molecules in general.<sup>2</sup> This development in theory calls for a parallel advancement on the side of experiment since quantitative experimental data, required to test the theoretical models, remain limited and somewhat fragmentary.<sup>3,4</sup> Finally, scientists have become increasingly concerned about the interaction of radiation (including electrons) with molecules (especially biomolecules). In particular, it is now appreciated that low energy

(<20 eV) electrons can cause, through electron attachment and dissociation processes, serious single- and double-strand breaks within DNA.<sup>5</sup> That work immediately focussed the attention of researchers in electron scattering physics to low energy electron scattering from some hydrocarbons, which can be considered as exemplar organic compounds, and from molecules which have similar structures as some structural elements of DNA. For example,  $C_2H_4$  was recently chosen by García and colleagues to be a test case for advancing their low energy particle track simulation code,<sup>6,7</sup> for modelling radiation damage in matter, with absolute differential and integral cross sections and energy loss spectra, such as we report later, being fundamental inputs for that simulation.

The electronic-state spectroscopy of ethylene has been investigated intensively (see Sec. II for more details),<sup>8–37</sup> but as we shall soon see it is not yet totally understood due to the overlapping of many Rydberg electronic states with each other and with the  $^1B_{1u}$  valence electronic state. This difficulty hence currently impedes a complete study on electron impact excitation of all the electronic states of ethylene. However, the lowest-lying excited electronic state ( $\tilde{a}^3B_{1u}$ ) of ethylene (see Fig. 1) is well resolved from the ground state and its other excited states, and it is therefore on this triplet state that we concentrate in this study. Differential cross sections (DCSS) for electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state have been theoretically calculated by Sun *et al.*,<sup>2</sup> using the Schwinger Multichannel (SMC) method. The SMC approach was also applied to this problem by Winstead and McKoy,<sup>38</sup> while Rescigno and Schneider<sup>39</sup> employed a

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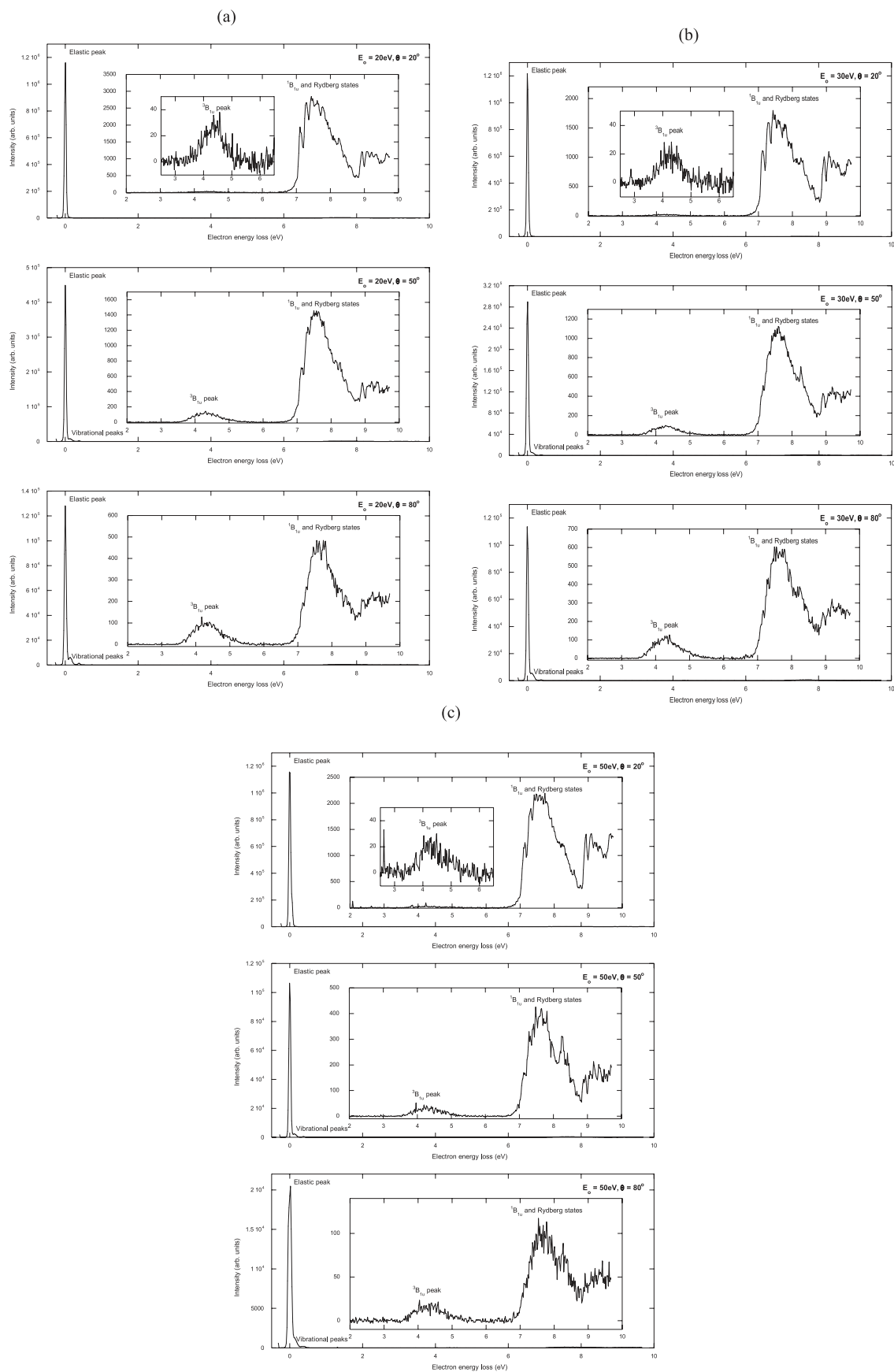


FIG. 1. Typical electron energy loss spectra of electron–ethylene scattering at (a) 20 eV, (b) 30 eV, and (c) 50 eV incident electron energy, obtained at a variety of kinematical conditions as denoted on the respective plots. They all clearly show the  $\tilde{a}^3B_{1u}$  peak being separated from the others. The  $^1B_{1u}$  state and the many overlapping Rydberg states form a strongly peaked band in all these spectra. Different scales were used to highlight the differences in the peaks' heights of the various components in these spectra, which vary with the kinematical conditions under study.

complex Kohn variational method (CKVM). While it is apparent that most of those theories agreed with each other quite well, in terms of the shapes and magnitudes of the DCSs, the theoretical models and current experimental results<sup>8,38,40</sup> were in poor accord in terms of the cross section magnitudes. This observation forms one rationale behind the present investigation.

Theorists<sup>2,39</sup> noted that the DCSs for the  $\tilde{a}^3B_{1u}$  electronic state of ethylene at near-threshold (see Table I) energies exhibit a *d*-wave character, with a broad minimum at around 90° scattering angle in the angular distribution. At somewhat

higher incident electron energies (to around ~12 eV), however, a clear backward peaking (typical of triplet excitation<sup>39,41</sup>) in the angular distribution developed. This behaviour was ascribed by Rescigno and Schneider<sup>39</sup> to be indicative for the importance of electron exchange in the low energy scattering dynamics of this excitation system. More recently, da Costa and co-workers<sup>42,43</sup> looked at the role played by polarisation effects in the calculation of the  $\tilde{a}^3B_{1u}$  DCSs. In particular, they investigated the influence of those effects in the energy range from threshold to 8 eV.<sup>43</sup> Comparison between their results, obtained from 2-channel SMC

TABLE I. Excitation energies of a selection of the electronic states in ethylene (eV). Numbers in parentheses are results from some of the different studies as denoted at the end of the table.

State	Nature	Theories								Expt. <sup>a,b,c</sup>
		Ballard <i>et al.</i> (SAC-CI) <sup>a</sup>	Huzinaga (SAC-CI) <sup>a</sup>	Foresman <i>et al.</i> (CIS) <sup>a</sup>	McMurchie and Davidson (CI) <sup>a,b,c</sup>	Buenker <i>et al.</i> (MRCI) <sup>a,b,c</sup>	Serrano- Andres <i>et al.</i> (PT2F) <sup>a</sup>	Nakatsuji (SACCI) <sup>a,b</sup>	Fischer- Hjalmar & and Kowalewski (SNE) <sup>c</sup>	
$1^1B_{3u}$	$3s$	7.17	7.15	7.1	7.26	7.13	7.17	7.33	7.49	7.11
$1^1B_{1g}$	$3p\sigma$	7.84	7.80	7.68	7.93	7.89 <sup>d</sup>	7.85	7.86	8.03	7.80 (7.83 <sup>b</sup> )
$1^1B_{2g}$	$3p\sigma$	7.87	7.85	7.83	8.01	7.86 <sup>d</sup>	7.95	7.93	8.19	7.90 (7.83 <sup>b</sup> )
$1^1B_{1u}$	$V(\pi, \pi^*)$	7.96	8.05	7.78	7.96	7.96 <sup>a,c</sup> (8.06 <sup>b</sup> )	8.40	8.17	...	7.65 <sup>b</sup> (7.6 <sup>c</sup> )
$1^1A_g$	$3p\pi$	8.23	8.2	8.10	8.36	8.21	8.40	8.28	8.42	8.28 <sup>a</sup> (8.26 <sup>b</sup> , 8.21 <sup>c</sup> )
$2^1B_{1g}$	$(\sigma, \pi^*)$	8.56	8.62	...	...	...	...	...	...	...
$2^1B_{3u}$	$3d\sigma$	8.68	8.66	8.71	8.80	8.73	8.66	8.90	8.98	8.62
$3^1B_{3u}$	$3d\delta$	8.88	8.85	...	8.99 <sup>b,c</sup>	9.31 <sup>a</sup> (8.92 <sup>b,c</sup> )	9.03	...	9.03	8.90
$1^1A_u$	$3d\pi$	8.89	8.86	...	8.99 <sup>b,c</sup>	9.04 <sup>a</sup> (8.83 <sup>b,c</sup> )	8.94	9.05	9.04	8.90 <sup>b</sup>
$1^1B_{2u}$	$3d\delta$	8.92	8.90	...	9.04 <sup>c</sup>	8.99 <sup>a</sup> (8.88 <sup>c</sup> )	9.18	...	9.04	8.90 <sup>a</sup>
$4^1B_{3u}$	$4s$	9.04	9.01	...	...	...	...	...	...	9.10 <sup>a</sup>
$2^1B_{1u}$	$3d\pi$	9.22	9.20	...	8.99 <sup>a</sup> (9.31 <sup>b,c</sup> )	...	9.31	9.44	...	9.33 <sup>a</sup> (9.36 <sup>b</sup> )
$1^1B_{3g}$	$(\sigma, 3s)$	9.57	9.54	...	...	...	...	...	...	9.51 <sup>a</sup>
$5^1B_{3u}$	$4d\sigma$	9.77	9.75	...	...	...	...	...	...	9.51 <sup>a</sup>
$2^1B_{2g}$	$(\sigma, \pi^*)$	9.91	9.90	...	...	...	...	...	...	...
$3^1B_{1g}$	$4p\sigma$	9.93	9.80	...	...	...	...	...	...	...
$3^1B_{2g}$	$4p\sigma$	10.16	10.06	...	...	...	...	...	...	...
$2^1B_{2u}$	$4d\delta$	10.09	10.09	...	...	...	...	...	...	9.62 <sup>a</sup>
$2^1A_u$	$4d\pi$	10.18	10.13	...	...	...	...	...	...	...
$1^3B_{1u}$	$T(\pi, \pi^*)$	4.34	4.43	3.54	4.49 <sup>b</sup>	4.35 <sup>a</sup> (4.46 <sup>b</sup> )	4.39	4.54	...	4.36 <sup>a</sup> (4.6 <sup>b</sup> )
$1^3B_{3u}$	$3s$	7.02	7.08	6.88	...	6.89 <sup>b,c</sup>	7.05	7.17	...	6.98 <sup>a,b</sup>
$1^3B_{1g}$	$3p\sigma$	7.76	7.8	7.60	...	7.62 <sup>b,c</sup>	7.80	7.85	...	7.79 <sup>a</sup> (7.78 <sup>b</sup> )
$1^3B_{2g}$	$3p\sigma$	7.79	7.87	7.72	...	...	7.90	7.85	...	7.78 <sup>b</sup>
$1^3A_g$	$3p\pi$	8.01	8.07	7.75	...	...	8.26	8.12	...	8.15
$2^3B_{1g}$	$(\sigma, \pi^*)$	8.10	8.29	...	...	...	...	...	...	...
$2^3B_{3u}$	$3d\sigma$	8.63	8.64	8.63	...	...	8.57	8.85	...	8.57
$3^3B_{3u}$	$3d\delta$	8.75	8.74	...	...	...	9.09	...	...	...
$1^3B_{2u}$	$3d\delta$	8.85	8.94	...	...	...	8.97	...	...	...
$1^3A_u$	$3d\pi$	8.85	8.99	...	...	...	8.94	8.97	...	...
$2^3B_{1u}$	$3d\pi$	8.99	9.44	...	...	...	9.07	9.07	...	...
$1^3B_{3g}$	$(\sigma, 3s)$	9.29	9.43	...	...	...	...	...	...	...
$^3B_{1u}$	...	...	...	...	...	...	...	9.17	...	...
$^1B_{1u}$	...	...	...	...	9.31 <sup>b,c</sup>	9.17 <sup>b,c</sup>	...	9.60	9.43	9.36 <sup>b</sup>

SAC-CI: Symmetry adapted cluster configuration interaction calculations; CIS: configuration interaction singles method; CI: configuration interaction method; MRCI: multi-reference configuration interaction method; PT2F: second order perturbation method; SNE: simple non-empirical method.

<sup>a</sup>Ballard *et al.*<sup>18</sup> and references therein.

<sup>b</sup>Nakatsuji<sup>19</sup> and references therein.

<sup>c</sup>Sension and Hudson<sup>20</sup> and references therein.

<sup>d</sup>There may be a "mix-up" between these two states as their positions are transposed, based on the results of Ballard *et al.*<sup>18</sup> and also based on the studies of Sension and Hudson<sup>20</sup> and Nakatsuji.<sup>19</sup>

calculations that either accounted for or ignored polarisation effects, showed a significant decrease in the magnitude of the DCSs, with only a minor change in their shapes, when polarisation was incorporated. Indeed when they compared their near-threshold  $\tilde{a}^3B_{1u}$  cross sections to the corresponding experimental data,<sup>8,40</sup> very good accord was now found. This level of agreement therefore demonstrated the crucial nature of also correctly including polarisation effects, when computing the  $\tilde{a}^3B_{1u}$  cross sections. Note that a similar effect was also found by da Costa *et al.*,<sup>44</sup> in their study of the excitation of electronic states in furan. It is important to note that all the SMC calculations referenced here<sup>2,38,42,43</sup> are two-channel (ground state and the  $\tilde{a}^3B_{1u}$  state) computations, while the CKVM results<sup>39</sup> were two-channel in the 4–9 eV energy range and three-channel (ground state,  $\tilde{a}^3B_{1u}$  state, and  $^1B_{1u}$  state) calculations thereafter up to 20 eV. We will return to the importance of this point later in Sec. IV.

In 1994 the first experiment to measure absolute differential cross sections for the electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state in  $C_2H_4$  was conducted by Allan,<sup>8</sup> in which DCS results at 5.68 eV, 7.18 eV, and 14.18 eV were reported. Subsequently, Asmis and Allan<sup>40</sup> revisited this system and reported excitation function measurements at the 0°, 90°, and 180° scattering angles. Finally Allan *et al.*<sup>38</sup> reported on some new extensive excitation function results, for energies from threshold to 18 eV and at the scattered electron angles 0°, 45°, 90°, 135°, and 180°. In addition, angular distribution data were published for the incident electron energies of 5.7 eV, 7 eV, and 15 eV. Again poor agreement ( $\sim$ a factor of 2) in the magnitude of the cross sections was found when those results<sup>38</sup> were compared to the earlier computations of Sun *et al.*<sup>2</sup> and Rescigno and Schneider.<sup>39</sup> However, an upgraded (in terms of the polarisation description) SMC calculation, also reported by Allan *et al.*,<sup>38</sup> gave a much better level of agreement in terms of the shape and magnitude of the DCS for near-threshold energies ( $\leq 7$  eV). That result is also consistent with the conclusions of da Costa and co-workers.<sup>42,43</sup> As all the available experimental data<sup>8,38,40</sup> comes from the one group at the University of Fribourg, another rationale for the present investigation is to provide an independent set of measurements for cross check and benchmarking purposes. Furthermore, we also extended the available data to higher (50 eV) incident electron energies, in that case with the modelling studies of García and colleagues in mind<sup>6,7</sup> but also to provide more data for theory to test against, which forms an additional reason for this study.

Integral cross sections (ICSs) for the lowest-lying triplet state of ethylene were first reported by Brongersma *et al.*<sup>45</sup> in the near-threshold region. This work showed a rapid linear rise in the magnitude of the ICS with increasing electron energy. Subsequently, van Veen<sup>46</sup> reported the  $\tilde{a}^3B_{1u}$  ICSs from threshold to around 14 eV. Van Veen found a relatively sharper rise in the data at the threshold region, compared to Brongersma *et al.*, and a resonance feature at around 1.4 eV above threshold. Note that both these measurements were made using the trapped-electron method.<sup>47</sup> The most recent experimental ICSs for this process can be found in Allan *et al.*,<sup>38</sup> at electron energies of 5.7 eV, 7 eV, and 15 eV, with an estimated uncertainty of  $\pm 25\%$  being cited on those

ICSs. From a theoretical perspective, ICSs due to Sun *et al.*,<sup>2</sup> Rescigno and Schneider,<sup>39</sup> Allan *et al.*<sup>38</sup> (at 5.75 eV and 7 eV), and da Costa *et al.*<sup>43</sup> are available in the literature. All these data will be compared against the present results later in this paper. Finally, for completeness, we also note the experimental total cross section measurements for electron– $C_2H_4$  scattering from Sueoka and Mori,<sup>48</sup> Szmytkowski *et al.*,<sup>49</sup> and Wickramarachchi *et al.*<sup>50</sup> While these works are perhaps not strictly relevant to the focus of this paper, total cross sections represent the sum of all the integral cross sections for the elastic and inelastic (including the  $\tilde{a}^3B_{1u}$ ) scattering processes and so therefore serve as a useful independent cross check for the validity of those data.

In Sec. II of this paper, we present some information on the excited electronic-state spectroscopy of  $C_2H_4$ , followed in Sec. III by a precis of our experimental methods and analysis details. Thereafter (Sec. IV), we provide our results and a discussion of those results before finishing with some conclusions.

## II. EXCITED-STATE SPECTROSCOPY OF ETHYLENE

Ethylene belongs to the symmetry group  $D_{2h}$  with three two-fold axes ( $C_2$ ) which are mutually perpendicular, three perpendicular planes of symmetry ( $\sigma$ ), and a centre of symmetry (i).<sup>51</sup> Planar ethylene has the x-axis defined perpendicular to the plane of the molecule, while the z-axis is along the C=C line.

The spectroscopy of  $C_2H_4$  has been extensively investigated since the early 1970s, both experimentally and theoretically, but even now, due to the highly overlapping nature of some of the excited electronic states (see Table I), some aspects remain unresolved. A summary of the results from some of those more significant earlier studies is given in Table I. In particular, with respect to the experimental work, many electron energy loss spectra of ethylene are available in the literature<sup>8–17</sup> although some of them were measured at a relatively low energy resolution. The present energy loss spectra (see Sec. III), with typical examples being given in Fig. 1, are often found to be in excellent qualitative or quantitative agreement with the results from some of those earlier works.<sup>8,14,15,17</sup> Similarly, results from the spectra given in Fig. 1 also correspond well with many of the theoretical results in Table I. The detailed energy loss spectra of Fig. 1, however, not only provide information on the spectroscopy of ethylene but also give information on the electron– $C_2H_4$  scattering dynamics. For example, relative to the elastic peak intensity, the low-lying  $\tilde{a}^3B_{1u}$  valence state increases in intensity as you go to lower incident electron energies and larger scattered electron angles. This behaviour is consistent with the excitation dynamics being largely due to the electron exchange interaction, as might be anticipated when a triplet state is excited from a singlet ground electronic state. Similarly, we also see in Fig. 1 that the  $^1B_{1u}$  valence state (see also Table I) increases its relative intensity as you go to smaller scattered electron angles and larger incident electron energies. This behaviour is consistent with the direct scattering process being the predominant excitation mechanism for that singlet state excitation.

The electronic states of ethylene were initially stated by Merer and Mulliken<sup>21</sup> to be formally similar to those of the hydrogen molecule, but with certain types of states that they labelled as the N, T, V, and Z valence states. These workers also noted the existence of many series of Rydberg states. In this nomenclature N is the “normal” state (electronic ground state:  $^1A_g$ ) with the electronic configuration ( $1\sigma_g$ ).<sup>2</sup> T is the lowest-lying triplet state ( $\tilde{a}^3B_{1u}$ ), while V is the lowest excited singlet valence state ( $^1B_{1u}$ ), both with the same configuration ( $1\sigma_g, 1\sigma_u$ ). Finally, the Z state has the configuration ( $1\sigma_u$ ).<sup>2</sup> This interpretation by Merer and Mulliken was largely consistent with the experimental electron spectra from Ross and Lassette.<sup>9</sup> In particular, the general structure of their<sup>9</sup> recorded spectra, similar to that reported in vacuum-ultraviolet (VUV) absorption experiments, affirmed that the electronic-state features of ethylene from 7–10.5 eV were complicated and a rather diffuse spectrum was thus observed.

In the late 1970s, Mulliken<sup>22,23</sup> continued his work on excitation of the electronic states in  $C_2H_4$ . He confirmed that its lowest excited valence states, which are formed when an electron from the highest filled  $\pi$  orbital ( $^1b_{3u}$ ) is excited to the lowest unoccupied  $\pi^*$  orbital ( $^1b_{2g}$ ), are the triplet (T) and singlet (V) states. For planar ethylene these correspond to the  $^3B_{1u}$  and  $^1B_{1u}$  states.<sup>22</sup> Subsequently, Mulliken also measured and assigned several other of the excited electronic states of  $C_2H_4$  and reported the first ionisation energy to be at 10.51 eV.<sup>23</sup> In this later work, however, the V state was now proposed to be “semi-Rydberg” in nature with a peak at 7.65 eV, a little lower in value than results from the calculations of McMurchie and Davidson<sup>24</sup> (at 7.96 eV) and Buenker *et al.*<sup>25</sup> (at 7.95 eV). The  $^1B_{2g}$ ,  $^1B_{3u}$ ,  $^1B_{1g}$ , and  $^1A_g$  states that were also assigned by Mulliken<sup>23</sup> lie, respectively, at 7.20 eV, 7.10 eV, 7.83 eV, and 8.26 eV, and they were all stated to be of a Rydberg type (see Table I).

The lowest triplet electronic state ( $\tilde{a}^3B_{1u}$ ) was at first defined to have its peak in the energy loss range 4.35 eV–4.86 eV,<sup>12,14,18,19,26</sup> but more recently this was specified to be at around 4.2 eV by Wilden and Comer,<sup>15</sup> Allan,<sup>8</sup> and Love and Jordan.<sup>17</sup> The present results (see Fig. 1) also showed the T-state to be at around 4.2 eV. This peak, which opens at  $\sim 3.4$  eV and ends at  $\sim 5.5$  eV, is well separated from the next low-lying excited states which open from  $\sim 7$  eV. Note that the vibrational structure of this triplet state was described by Wilden and Comer.<sup>15</sup> In addition to their report on details of the T-state, Wilden and Comer<sup>16</sup> also published high resolution (25–40 meV) energy loss spectra covering the energy loss range 6–11 eV. These results also confirmed a number of the optically observed Rydberg states seen in the previous studies.

Nakatsuji<sup>19</sup> calculated and summarised relevant ethylene vertical excitation energies in the  $B_{1u}$  symmetry, which included some of the Rydberg state excitation energies. He compared the results from his work with the theoretical data of Buenker and co-workers<sup>25,27–31</sup> and Brooks and Schaefer,<sup>32</sup> and the experimental results of McMurchie and Davidson<sup>24,33</sup> with most of these data being summarised in Table I. Generally, the results from Nakatsuji<sup>19</sup> only qualitatively corresponded (in terms of the energies of the states) with the ex-

perimental values suggesting that a more sophisticated target description for ethylene was still required. Note that the VUV resonance Raman study results from Sension and Hudson<sup>20</sup> are also included in Table I.

More recently, Ballard *et al.*<sup>18</sup> reported results from their calculations of the valence and Rydberg electronic states of  $C_2H_4$  using symmetry adapted cluster configuration interaction (SAC-CI) methods in conjunction with large atomic natural orbital and Huzinaga basis sets.<sup>18</sup> Their work confirmed that the V state ( $^1B_{1u}$ ) was responsible for the broad diffuse absorption band observed by Sension and Hudson<sup>20</sup> with a maximum at around 7.6 eV. Detailed descriptions for the nature (assignments) of some of the states in Table I can also be found in Ballard *et al.*

Another important study into the spectroscopy of ethylene was the energy loss spectra obtained by Love and Jordan,<sup>17</sup> at constant residual energies from 0.08 eV to 0.41 eV. This method revealed sharp features in their spectra, which could then be assigned to several of the electronic states. In particular, the obvious peaks at 6.98 eV, 7.78 eV, 8.26 eV, and 8.62 eV in their spectra<sup>17</sup> are in very good agreement with those from previous experiments (see Table I). However, several other peaks were observed by these authors for which there were no corresponding features of comparable intensity in the optical spectra, suggesting that these features arise from optically forbidden transitions. In addition to the studies described above, there are a number of other articles which also report excitation energies of the electronic states of  $C_2H_4$ . Those investigations all show minor variations in the electronic-state positions in comparison with the data in Table I. For example, the calculation of Rescigno and Schneider<sup>39</sup> found the T-state threshold to be at 3.64 eV, while that from da Costa *et al.*<sup>43</sup> was at 3.6 eV. Nonetheless, as these variations are minor these further studies<sup>29,34–37</sup> are not described here.

The important point of the above discussion on the spectroscopy of  $C_2H_4$ , in relation to this paper, is that the lowest-lying  $\tilde{a}^3B_{1u}$  electronic state of ethylene is well resolved from the other valence and Rydberg excited electronic states and also from the vibrational levels of the ground electronic state (see also Fig. 1). Therefore, one of the major complicating factors in determining absolute cross sections for excitation of electronic states in molecules,<sup>52</sup> namely, the strongly overlapping nature of many of the vibrational sub-levels of these electronic states, even in relatively simple species like  $H_2$  (Ref. 53) and  $N_2$ ,<sup>54</sup> is not an issue in this study.

### III. EXPERIMENTAL METHODS AND ANALYSIS DETAILS

A high-resolution electron monochromator, described originally by Brunger and Teubner,<sup>55</sup> was employed to make the present measurements. Here, a high-purity ethylene beam (Aldrich Chemical Company, stated purity >99.5%), effusing from a molybdenum tube of  $\sim 0.6$  mm internal diameter, is crossed with a beam of pseudo-monoenergetic electrons of desired energy  $E_0$ . Elastically and inelastically scattered electrons at a particular scattering angle  $\theta$  are energy analysed and detected. The overall energy resolution of the monochromator

was  $\sim 50$ – $60$  meV (full width at half maximum, FWHM) and, under normal operating conditions, incident electron beam currents in the range  $\sim 2$ – $4$  nA were obtained in the interaction region for the energy range of our measurement. As in previous work,<sup>55</sup> the true zero scattering angle was determined as that about which the elastic scattering intensity was symmetric. The estimated error in this determination is  $\pm 1^\circ$ . The electron energy scale was calibrated against the well-known helium  $^2S$  resonance at 19.367 eV (Ref. 56) and is estimated to be accurate to less than 50 meV.

At each incident electron energy in the range  $E_0 = 9$ – $50$  eV, energy loss spectra, at each scattering angle in the range  $\theta = 15^\circ$ – $90^\circ$ , were recorded over the range  $\sim -0.5$  eV to 9.8 eV. Typical spectra (with the background having already been subtracted) are shown in Fig. 1, where the  $\tilde{a}^3B_{1u}$  valence electronic state is clearly separated from the elastic and ground-vibrational transitions and the Ryberg and  $^1B_{1u}$  valence electronic states. The energy-loss spectra were obtained by ramping the analyser in an energy-loss mode in conjunction with a multichannel scalar (TN-7200), which stored the scattered signal as a function of energy loss. The data were then transferred to a 433 MHz workstation for analysis. Each spectrum was then analysed (deconvolved) by a least squares fitting technique that is similar in detail to that outlined by Nickel *et al.*,<sup>57</sup> although adapted to accommodate the particular spectroscopy of ethylene. In particular, the Franck-Condon line profile of the  $\tilde{a}^3B_{1u}$  peak of ethylene was found to be rather asymmetric. To account for this, and to ensure all the  $\tilde{a}^3B_{1u}$  electronic-state intensity was captured, two Gaussian functions were regularly employed in the spectral fit to that state. In practice, the fitting procedure yielded the ratio ( $R$ ) of the DCS for the  $\tilde{a}^3B_{1u}$  state of interest,  $\sigma_{3B_{1u}}(E_0, \theta)$ , to that for the elastic DCS,  $\sigma_0(E_0, \theta)$ , i.e.,

$$R(E_0, \theta) = \frac{\sigma_{3B_{1u}}(E_0, \theta)}{\sigma_0(E_0, \theta)}. \quad (1)$$

It is immediately apparent from Eq. (1) that the product  $R(E_0, \theta) \times \sigma_0(E_0, \theta)$  then gives the required  $\tilde{a}^3B_{1u}$  DCS provided  $\sigma_0(E_0, \theta)$  is known. In the present study our preferred elastic ethylene differential cross sections are those obtained by Panajotovic *et al.*,<sup>58</sup> although we note that their results are largely consistent with those from the independent studies of Khakoo *et al.*<sup>59</sup> and Allan *et al.*<sup>38</sup> Hence, we are confident in their<sup>58</sup> validity. Equation (1) is only valid if the transmission efficiency of the analyser remains constant over the energy loss and the angular range studied, or is at least well characterised. In this work we determined the behaviour of the analyser response function following the philosophy outlined by Allan.<sup>60</sup>

Particular attention to the identification and quantification of all possible sources of error have been made throughout these measurements, with a general discussion of these sources of error being found in the work of Brunger and Buckman.<sup>61</sup> In this case the statistical errors associated with the scattering intensity measurements are small ( $\leq 2\%$ ). Additional errors due to the uncertainty in the elastic DCSs (Ref. 58) ( $\sim 15\%$ ) and our transmission calibration ( $\sim 20\%$ ) must also be considered. As a result the overall errors on our

DCS typically range from 25%–32%, depending on the  $E_0$  and  $\theta$  in question.

Finally, the measured  $\tilde{a}^3B_{1u}$  DCSs are extrapolated to  $0^\circ$  and  $180^\circ$ , using a molecular phase shift analysis (MPSA) technique,<sup>62</sup> before performing the usual integration in order to determine the ICSs at each  $E_0$  for this state. Because of the uncertainty in performing this extrapolation, particularly between the backward angles  $90^\circ$ – $180^\circ$ , the overall errors on our ICSs are typically in the range  $\sim 30\%$ – $45\%$ . Note, however, the available backward angle DCS data from Allan and colleagues<sup>8,38,40</sup> does help us perform the extrapolations in this case to some degree.

#### IV. RESULTS AND DISCUSSION

In Table II and Fig. 2 we list and plot the present differential cross sections for electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state in ethylene. Also included in Table II are our estimates of the errors on those DCSs, with all uncertainties being cited at the one standard deviation level. In Fig. 2 we also plot all relevant corresponding data from the University of Fribourg group,<sup>8,38,40</sup> Kohn variational theory results from Rescigno and Schneider,<sup>39</sup> and the Schwinger multichannel results from the Caltech group.<sup>2,38</sup>

As is clearly shown in Fig. 2, there are generally no significant differences between our results and the previous measured data of Allan and colleagues,<sup>8,38,40</sup> when the uncertainties on the various data sets are taken into account. In particular, at 9 eV, 11 eV, 18 eV, and in a more limited fashion at 20 eV, the present DCSs showed quite excellent agreement with those of Allan *et al.*<sup>38</sup> Even at 14.5 eV, where

TABLE II. Differential cross sections ( $\times 10^{-19}$  cm<sup>2</sup>/sr) for electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state in C<sub>2</sub>H<sub>4</sub>. Numbers in parentheses are the percentage errors on the data.

$\theta_e$ (°)	Energy (eV)						
	9	11	14.5	18	20	30	50
15	20.153 (30.50)	8.837 (42.86)	3.340 (25.79)	2.517 (28.25)	3.867 (25.13)	...	...
20	15.938 (25.83)	8.790 (42.35)	2.764 (26.12)	2.846 (29.32)	3.673 (25.15)	2.291 (25.63)	1.102 (25.31)
30	14.619 (26.16)	8.981 (29.05)	4.747 (26.68)	4.408 (25.57)	4.894 (26.07)	3.224 (26.10)	1.813 (26.32)
40	10.659 (25.08)	9.001 (31.52)	3.177 (25.12)	3.900 (25.22)	4.959 (25.37)	3.279 (26.16)	1.974 (25.12)
50	9.343 (25.46)	7.988 (29.56)	3.252 (26.16)	3.157 (27.76)	4.589 (25.14)	3.539 (25.24)	1.757 (25.17)
60	12.397 (25.64)	10.026 (26.03)	3.419 (26.32)	3.859 (25.49)	4.693 (25.12)	3.475 (25.08)	1.826 (25.18)
70	16.054 (28.80)	14.023 (26.91)	4.810 (27.16)	5.085 (26.32)	5.733 (25.10)	3.261 (25.11)	1.658 (25.09)
80	17.678 (30.20)	18.104 (26.64)	6.384 (25.08)	6.613 (25.09)	6.183 (25.31)	3.147 (25.12)	1.354 (25.84)
85	...	...	6.670 (27.62)	5.474 (25.17)	...	...	...
90	18.254 (25.80)	21.122 (28.35)	...	...	7.829 (25.27)	2.984 (25.59)	1.342 (25.26)

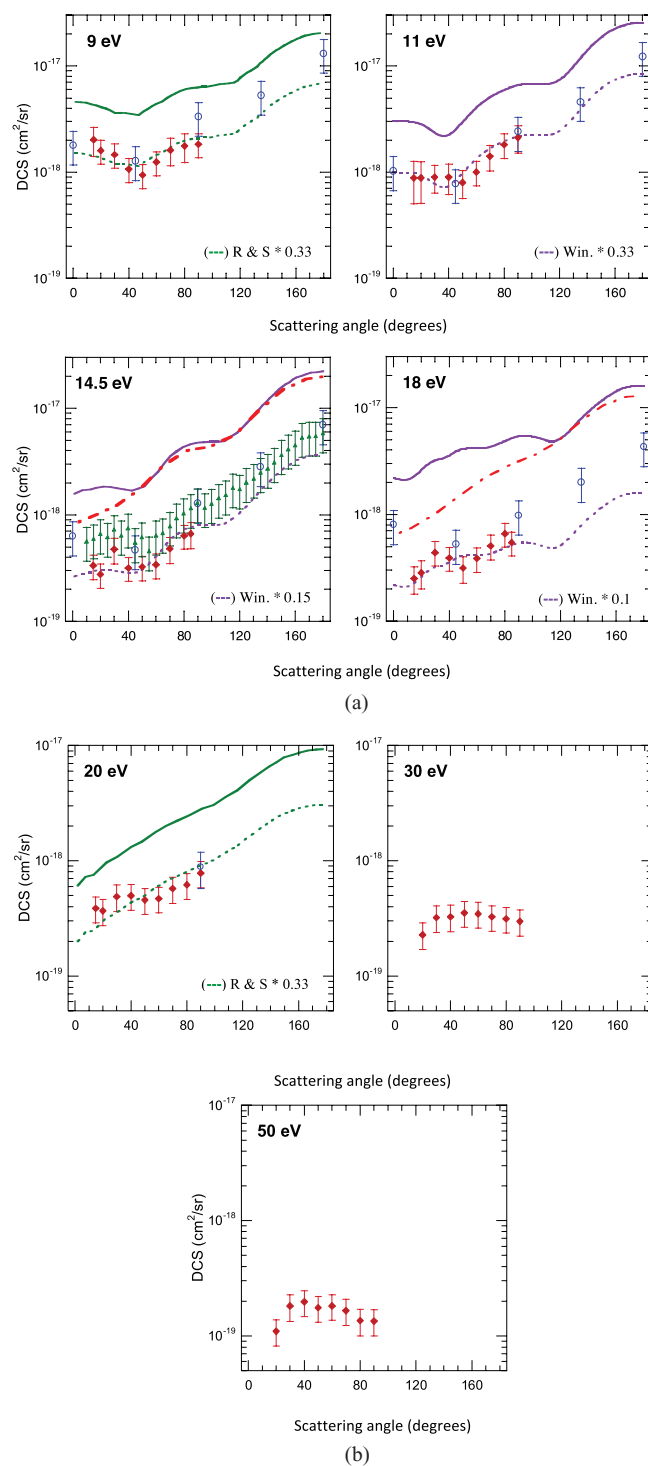


FIG. 2. (a) Differential cross sections ( $\text{cm}^2/\text{sr}$ ) for electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state of  $C_2H_4$  at the given incident electron energies. ( $\blacklozenge$ ) Present data, ( $\circ$ ) Allan,<sup>38</sup> ( $\blacktriangle$ ) Allan (at 15 eV),<sup>38</sup> (—) Rescigno and Schneider (at 9 and 20 eV),<sup>39</sup> (—) Winstead and McKoy (at 11, 14.5, and 18 eV).<sup>2,40</sup> The dashed lines present the theoretical data multiplied by the given values in order to facilitate a comparison of the respective angular distributions. Also shown are 15 eV and 18 eV data from Rescigno and Schneider.<sup>39</sup> (— — —). (b) Same as in Fig. 2(a), but at 20, 30, and 50 eV incident electron impact energies.

the level of agreement is somewhat less impressive, we would argue that the DCSs from the two groups are still consistent. Indeed, one reason why there is more of a difference here is that while our measurement was performed at 14.5 eV,

that of Allan *et al.* was conducted at 15 eV. Note that the agreement between the present data and the earlier 14.5 eV data from Asmis and Allan<sup>40</sup> is very good. Thus, from these plots, we have effectively confirmed the results of Allan and co-workers in the 9–20 eV energy range. This is quite a remarkable result in the context of excitation of electronic states in molecules by electron impact, where in general (although there has been some recent improvement of our understanding in  $N_2$ <sup>54</sup>) agreement between available experimental cross sections is often “patchy” at best.<sup>4,52</sup> This leads us to suggest that excitation of the  $\tilde{a}^3B_{1u}$  electronic state in  $C_2H_4$  might now well be considered to have been experimentally benchmarked, thus making it an excellent scattering system for theorists to study and test their approximations against. At our higher incident electron energies (30 eV and 50 eV), we unfortunately do not have any relevant theory or data to compare against. Nonetheless, we considered it important to extend the energy range of the available DCS data against which higher-level theories might ultimately be tested against, and to provide relevant data for the foreshadowed charged particle track simulations in ethylene from the Madrid group.<sup>6,7</sup> The present DCSs at 30 eV and 50 eV showed a significant reduction in magnitude compared to the cross sections at the lower energies. Moreover, the data at these energies also indicated an obvious change in their angular distributions (shapes), being almost pseudo-isotropic over much of the measured scattered electron angular range. This contrasts to the angular distributions in the 9–20 eV energy range, where the DCSs are largely seen to monotonically increase in magnitude with increasing scattering angle. As noted by Rescigno and Schneider,<sup>39</sup> such angular distributions are consistent with electron exchange playing a dominant role in the scattering dynamics.

From a theoretical perspective, all the DCS calculations gave results that were significantly greater in magnitude at each energy studied, compared to the experimental values (see Fig. 2). In terms of the shapes of the angular distributions, however, excellent agreement is found at 9 eV and 20 eV when the Kohn variational method results are scaled by a factor of 0.33. Note that at 9 eV the Kohn calculation was a 2-channel one, while at 20 eV three channels were included in the scattering description. A similar story is also found with the SMC results, in this case at 11 eV, 14.5 eV, and 18 eV the shape agreement is very good when the theory is, respectively, scaled by the factors 0.33, 0.15, and 0.10 (again see Fig. 2). The most likely explanation for this latter observation, at least in part, is that the two-channel (ground electronic-state and  $\tilde{a}^3B_{1u}$ -state) formalism exclusively employed by the SMC approach increasingly fails as one goes to energies further removed from the  $\tilde{a}^3B_{1u}$  threshold energy, when more channels become physically open. Support for this assertion can be seen in the three-channel CKVM result at 20 eV, needing a 0.33 scaling factor to give agreement with the data, compared to the 18 eV two-channel SMC result where a scaling factor of 0.1 was required before accord with the measured data was found. To further investigate the reasons for the disagreement between the theoretical and experimental results the significant role played by the target polarization effect in the calculation of the excited state DCSs was



TABLE III. Integral cross sections ( $\times 10^{-17}$  cm $^2$ ) for electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state in C $_2$ H $_4$ . Numbers in parentheses are the percentage errors on the data.

Energy (eV)	ICS ( $\times 10^{-17}$ cm $^2$ )
9	4.758 (35.12)
11	4.585 (45.30)
14.5	2.267 (34.24)
18	1.663 (34.16)
20	1.279 (30.01)
30	0.311 (42.60)
50	0.134 (36.22)

probed in detail by da Costa and co-workers<sup>42,43</sup> In particular, they investigated the influence of this effect on the excitation of the  $\tilde{a}^3B_{1u}$  state in the energy range from threshold to 8 eV.<sup>43</sup> Comparison between their 2-channel SMC results, with and without the correction for polarisation effects, showed a significant decrease in the magnitude of the DCSs with only a minor change in shape, when polarisation was incorporated. In fact, when their 2-channel SMC plus polarisation results were compared with the experimental cross sections,<sup>8,40</sup> near-threshold, very good agreement was now found. This new level of agreement therefore also clearly demonstrated the important nature of getting the target polarisation description correct, in computing excited-state cross sections in molecules.<sup>42,43</sup>

In Table III we list our derived ICSs, obtained using a MPSA analysis,<sup>62</sup> along with their associated error bars. Note that once again these errors are quoted at the one standard deviation level. These data, along with the earlier near-threshold measurements of Brongersma *et al.*<sup>45</sup> and van Veen<sup>46</sup> and results from Allan *et al.*<sup>38</sup> at the three energies of 5.7 eV, 7 eV, and 15 eV, are plotted in Fig. 3. Also plotted in Fig. 3 are the CKVM results from Rescigno and Schneider,<sup>39</sup> an early SMC computation from Sun *et al.*,<sup>2</sup> a later SMC result, only at 5.75 eV and 7 eV, from Allan *et al.*,<sup>38</sup> and an independent SMC calculation from the Brazilian group.<sup>43</sup> Given our description at the DCS level, it is not surprising that the SMC theory of Sun *et al.*<sup>2</sup> and the CKVM theory of Rescigno and Schneider<sup>39</sup> gave ICSs that are too high in magnitude compared to the present data and that of Allan *et al.*<sup>38</sup> The trapped-electron ICS of van Veen<sup>46</sup> also appear to be too high in magnitude, although the trend in similar data from Brongersma *et al.*<sup>45</sup> does appear consistent with the present results. The more recent SMC results by Allan *et al.*<sup>38</sup> and the experimental ICS from Allan *et al.*, also appear to be in good accord with our measurements, albeit over a limited energy range. However, unlike at the DCS level, more experimental studies are needed at the ICS level before any claim of this scattering system being benchmarked could be contemplated. Nonetheless the present ICS, extrapolated to threshold using (for example) the results of Brongersma *et al.*, do form a useful database for incorporation by García and colleagues into their charged particle track simulations in ethylene.

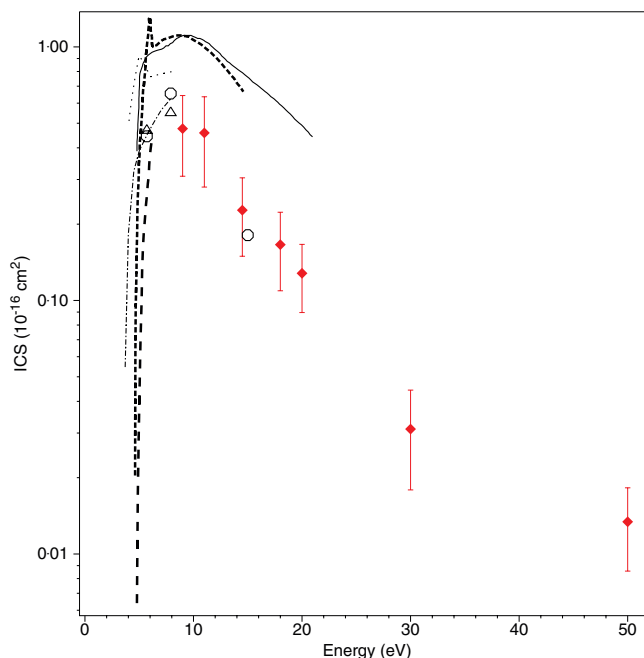


FIG. 3. Integral cross sections ( $10^{-16}$  cm $^2$ ) for electron impact excitation of the  $\tilde{a}^3B_{1u}$  electronic state in C $_2$ H $_4$ . Present data ( $\blacklozenge$ ), and results from other calculations and measurements due to Sun *et al.*<sup>2</sup> (—), van Veen<sup>46</sup> (---), Brongersma *et al.*<sup>45</sup> (---), Allan *et al.* (expt. —  $\circ$ ) and (SMC —  $\triangle$ ),<sup>38</sup> da Costa *et al.*<sup>43</sup> (— · — ·), and Rescigno and Schneider<sup>39</sup> (· · · ·) are also shown.

## V. CONCLUSIONS

We have reported on our extensive series of energy loss and differential and integral cross section measurements, for electron impact excitation of the  $\tilde{a}^3B_{1u}$  excited electronic state in C $_2$ H $_4$ . All these data form an important element for the foreshadowed charged particle track simulations in ethylene by García and colleagues. The present DCSs were found to be in very good accord with independent data from Allan and his collaborators,<sup>8,38,40</sup> in the energy range 9–20 eV, leading us to speculate that at the differential cross section level this scattering system might be considered as having been experimentally benchmarked. As excitation of the  $\tilde{a}^3B_{1u}$  state needs both a good description of the exchange interaction and a good description of the target polarisation, in order to correctly compute the cross sections, it represents an excellent system against which theories might test how they incorporate for those effects. Finally, we note that the present investigation also extended the availability of both differential and integral cross sections for the  $\tilde{a}^3B_{1u}$  valence state, from 20 eV to 50 eV.

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