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Low-energy electron scattering from C_4H_9OH isomers

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We present differential, integral, and momentum-transfer cross sections for elastic scattering of low-energy electrons by three butanol isomers, isobutanol, *t*-butanol, and 2-butanol. Our results were calculated with the Schwinger multichannel method in the static-exchange plus polarization approximation for collision energies from 1 to 50 eV. The present results are compared with previous calculations and measurements for the remaining C_4H_9OH isomer, *n*-butanol [Khakoo *et al.*, Phys. Rev. A **78**, 062714 (2008)]. Distinctive behavior is observed in the differential cross sections at collision energies between 5 and 10 eV. In particular, whereas *n*-butanol exhibits an *f*-wave scattering pattern, the other isomers exhibit *d*-wave behavior. A similar pattern is found in the related alkanes when comparing straight-chain versus branched isomers. We discuss the possible connection of this behavior to shape resonances that influence the scattering.

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I. INTRODUCTION

Studies of electron collisions with families of related molecules provide an opportunity to gain insights into the collision physics that are less apparent in studies of a single molecule. For example, recent work by Allan and co-workers on various alcohols [1] indicated the presence of an O–H σ^* resonance whose influence on low-energy dissociative attachment increased with the size of the molecule, while similar studies [2] of asymmetric ethers revealed pronounced energy selectivity in which C–O bond is broken, as well as a general tendency against breaking O–CH_3 bonds. Such results give clues about where on the molecule the impinging electron attaches to form a resonance (temporary anion) and about which molecular features—for example, the size, the presence or absence of substituent groups, and the arrangement of atoms—are most significant in determining the electron-scattering behavior and subsequent nuclear dynamics.

In this paper we build upon our earlier studies of the straight-chain alkyl alcohols from methanol (CH_3OH) [3] through normal or *n*-butanol (C_4H_9OH) [4] by considering all three of the remaining isomers of butanol that are obtained from *n*-butanol by moving the OH group from its terminal position and/or changing the carbon chain from straight to branched: 2-butanol, also known as *sec*-butanol or butan-2-ol; isobutanol or 2-methylpropan-1-ol; and *tert*-butanol, hereafter called *t*-butanol and also known as 2-methyl-2-propanol (Fig. 1). Our goal is to identify and, as far as possible, account for features that are common across the butanols as well as features that differ among them and to relate the electron-scattering behavior of the butanols both to that of the corresponding alkanes (in which OH is replaced by H) and to that of the smaller alcohols. At the same time, our calculations produce quantitative values for the elastic cross sections that may be of relevance in modeling electron transport during spark or corona-discharge ignition of the butanols, which have attractive properties as potential biofuels (e.g., [5,6]).

The remainder of this paper is organized as follows. In Sec. II we describe aspects of the theoretical approach relevant to the present calculations. In Sec. III we present and discuss our results, and we close in Sec. IV with a brief summary of those results.

II. THEORY

Our calculations of the cross sections employed the Schwinger multichannel (SMC) method. Both the SMC method and its implementation for parallel computers have been described elsewhere [7], so here we discuss only the points that are relevant to the present calculations.

In order to keep the calculations for isobutanol, 2-butanol, and *t*-butanol comparable to previous calculations for *n*-butanol, we followed the same procedures as described in Ref. [4]. Although these molecules may exist in various conformations, to facilitate the calculations we required C_s point-group symmetry (that is, a reflection plane) except in 2-butanol, whose chiral center precludes mirror symmetry. Subject to those symmetry constraints, we optimized the molecular geometries using the electronic structure package GAMESS [8] by minimizing the ground-state energy at the MP2/6-31G(d) level of approximation, that is, second-order Möller-Plesset perturbation theory within the 6-31G(d) contracted Gaussian basis set as contained in GAMESS. At the optimized geometries, we computed single-configuration self-consistent field (SCF) wave functions for the molecules' ground electronic states using the DZV++($2d$,$1p$) basis set (where DZV denotes double-ζ valence) as contained in GAMESS, as in Ref. [4]. The molecular structures for the four isomers are shown in Fig. 1. The computed electric dipole moments and the symmetry group for each isomer are shown in Table I.

Many conformers of *n*-butanol are predicted to lie within 1 kcal/mol of the lowest-energy form [10], which has C_1 symmetry, and multiple conformers are observed in the gas phase and in a supersonic jet expansion [11]. Multiple conformers of nearly equal energy can likewise be expected for each of the butanol isomers considered here. By restricting our studies to a single conformer that is not necessarily the lowest-energy species, we are implicitly assuming, as in previous work [4], that conformational effects on the elastic electron cross section are minor. The good overall comparison with experimental data found for the straight-chain alcohols studied previously [3,4] suggests that this assumption may be valid.

Our scattering calculations were done at the static-exchange plus polarization level of approximation. In the SMC method, both short-range correlation and long-range polarization

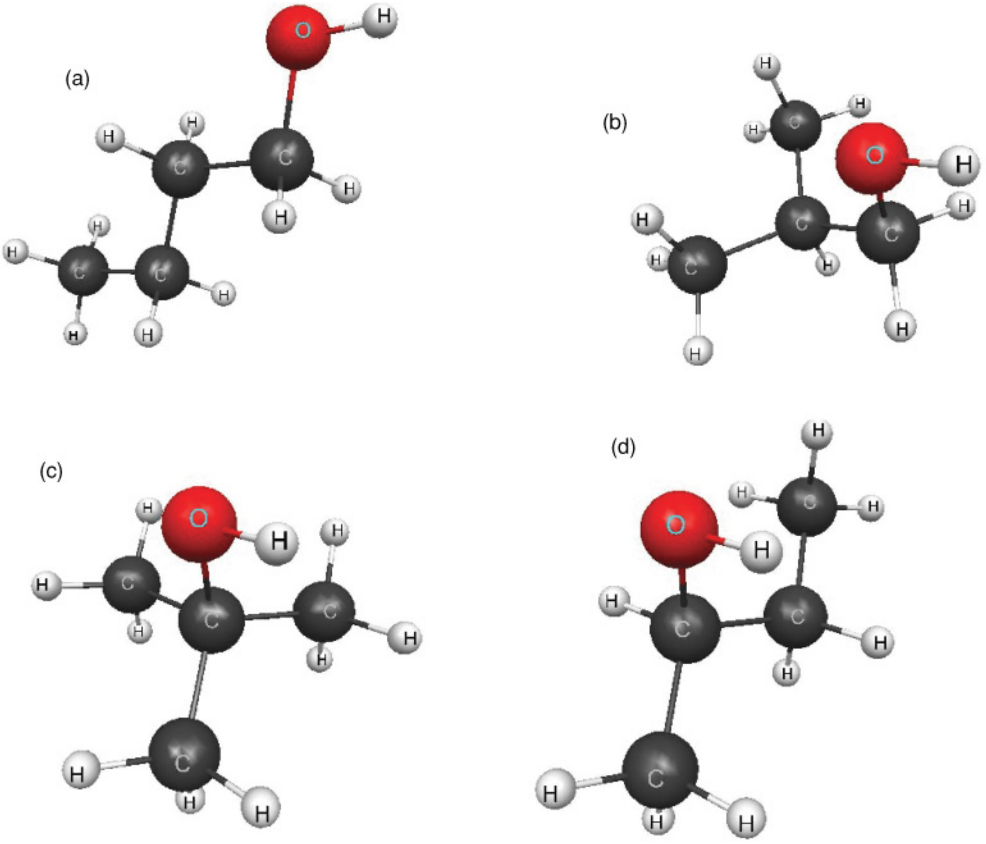

FIG. 1. (Color online) Geometrical structure of C_4H_9OH isomers: (a) n-butanol, (b) isobutanol, (c) t-butanol, and (d) 2-butanol (generated using MACMOLPLT [9]).

effects are taken into account through single (virtual) excitations of the target molecule's ground electronic state that are properly antisymmetrized with a one-electron function ("scattering orbital"). In the present case, the "particle" orbitals into which target electrons are virtually excited and the scattering orbitals describing the extra electron are both drawn from the space of virtual (unoccupied) orbitals produced in the SCF/DZV++($2d$,$1p$) calculation for the target's ground state. For efficiency's sake it is important to have a rapidly convergent description of correlation and polarization effects. To this end we applied an orthogonal transformation within the virtual-orbital space to generate modified virtual orbitals (MVOs) [12] using a cationic Fock operator with charge equal to +6, as in [4]. Excitations into the lowest-energy MVOs, which are compact, valencelike, and localized near the target, usually give a good description of correlation and polarization effects [13]. In the present work we included singlet-coupled excitations from the 10 highest-energy valence occupied orbitals into the 20 lowest MVOs and used all MVOs as scattering orbitals. For isobutanol and t-butanol, the resulting A' and A'' variational spaces contained, respectively, 14 541 and 14 513 doublet configuration state functions (CSFs) for a total of 29 054, while for 2-butanol, 29 054 CSFs made up a single variational space.

TABLE I. Symmetry groups used in our calculations and the computed dipole moments (Debye) for the C_4H_9OH isomers.

System	Group	μ
n-Butanol	C_s	1.746
Isobutanol	C_s	1.690
t-Butanol	C_s	1.773
2-Butanol	C_1	1.814

The body-frame angular distributions were averaged over molecular orientations to obtain laboratory-frame differential cross sections for a gas of randomly oriented molecules.

III. RESULTS AND DISCUSSION

In Figs. 2 and 3 we show the integral and momentum-transfer cross sections for the four isomers of C_4H_9OH; theoretical and experimental results for n-butanol are taken from Ref. [4]. The computed cross sections for the four isomers are similar in shape but differ somewhat in magnitude, especially at lower energies. The increase of both the integral and the momentum-transfer cross sections at low impact energies is characteristic of molecules with a permanent electric dipole moment, which produces a long-range potential that can weakly scatter electrons at large impact parameters. The cross sections of all four molecules also exhibit a broad maximum at about 10 eV, similar to that seen in the alkanes, including n-butane and isobutane [14].

Figure 4 shows the present differential cross sections at 1, 2, 5, 10, 15, 20, 30, and 50 eV, with theoretical and experimental

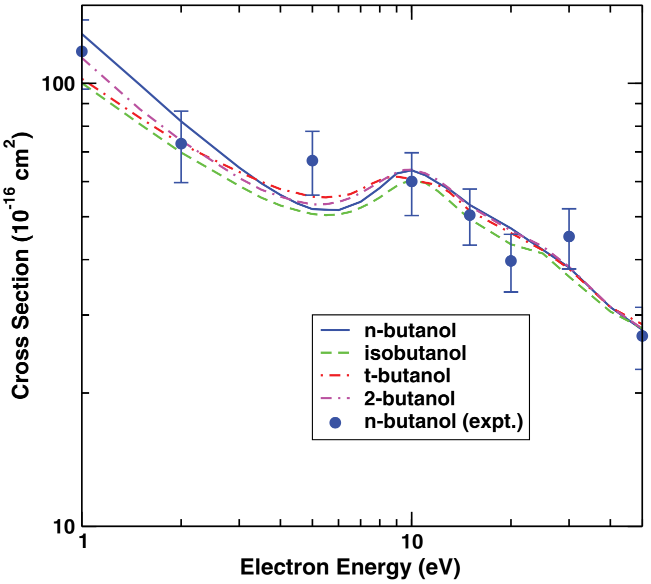

FIG. 2. (Color online) Integral cross sections for the C_4H_9OH isomers. The results for *n*-butanol are from Ref. [4].

results for *n*-butanol [4] again included for comparison. At small scattering angles, the differential cross sections for all four isomers are similar at all energies and increase strongly in the forward direction due to the long-range scattering by the dipole potential mentioned previously. At larger angles, the differential cross sections exhibit oscillations characteristic of either *d*- or *f*-wave scattering [15], depending on the isomer, roughly in the 6 to 10 eV energy range. To illustrate this aspect in more detail, differential cross sections from 6 to 10 eV are shown at 1-eV intervals for *n*-butanol and isobutanol in Fig. 5, along with previously obtained results for the corresponding isomers of C_4H_{10}, *n*-butane and isobutane [14], while cross sections for 2-butanol and *t*-butanol are shown in Fig. 6. There is a marked qualitative resemblance between the cross sections of *n*-butane and *n*-butanol, both of which exhibit an *f*-wave pattern, with a pronounced minimum near 90° flanked by two more minima (or at least plateaus, as in *n*-butane). The cross section of isobutanol also resembles that of the corresponding alkane, isobutane, but in this case the scattering pattern is *d* wave rather than *f* wave, with a maximum rather than a minimum near 90°. As seen in Fig. 6, the differential cross sections for 2-butanol and *t*-butanol are also primarily of *d*-wave type, although the first minimum is only a plateau in 2-butanol, while in *t*-butanol a third minimum near 45° grows in by 10 eV.

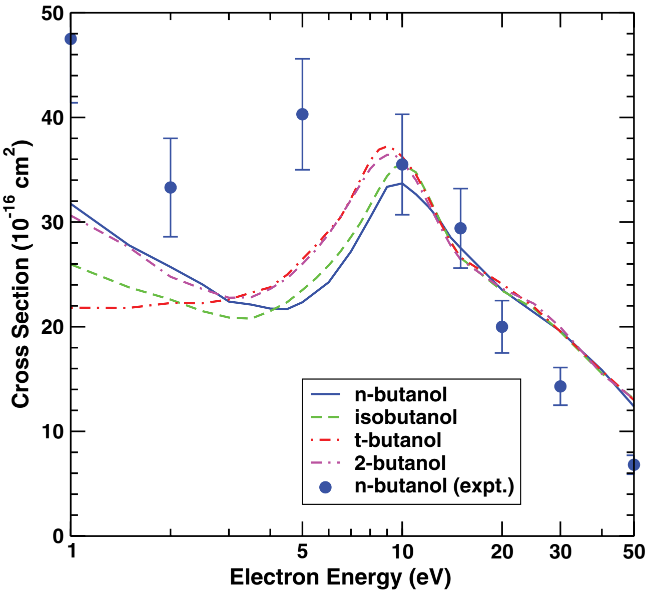

FIG. 3. (Color online) Momentum-transfer cross sections for the C_4H_9OH isomers. The results for *n*-butanol are from Ref. [4].

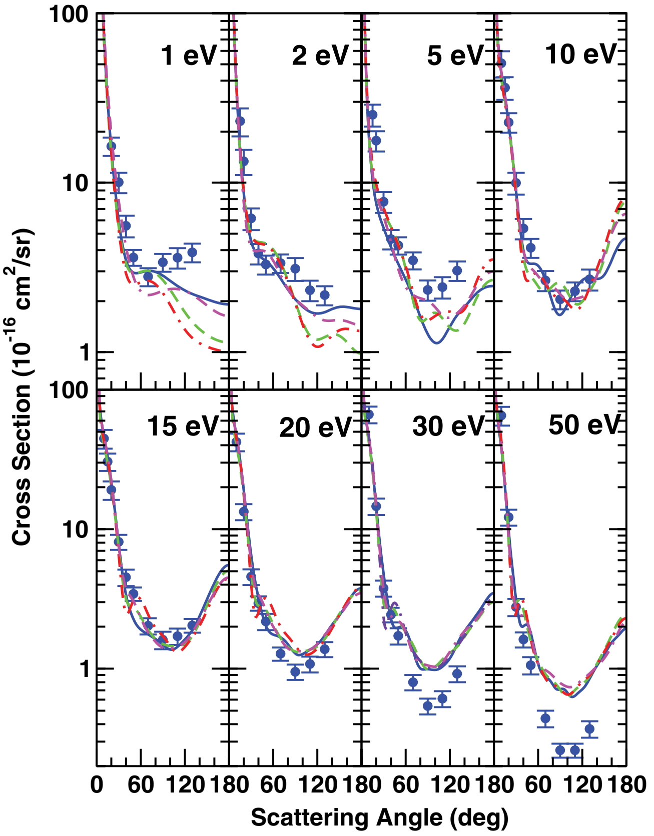

FIG. 4. (Color online) Differential cross sections for the C_4H_9OH isomers. Solid (blue) line, *n*-butanol; dashed (green) line, isobutanol; dot-dashed (red) line, *t*-butanol; and dot-dot-dashed (magenta) line, 2-butanol. The blue bullets correspond to the experimental data for *n*-butanol from Ref. [4].

As remarked previously [4], the *f*-wave scattering pattern exhibited by the straight-chain isomers *n*-butane and *n*-butanol is also found in smaller alkanes and alkyl alcohols, namely, ethane (C_2H_6), propane (C_3H_8), ethanol (C_2H_5OH), and *n*-propanol (C_3H_7OH), yet the smallest alkane and alcohol of all (methane, CH_4, and methanol, CH_3OH) show a *d*-wave pattern. Summarizing these observations together with the present results, we note that the general trend is that the straight-chain systems (ethane, ethanol, propane, *n*-propanol, *n*-butane, and *n*-butanol) exhibit *f*-wave scattering behavior in the 5 to 10 eV energy range, while the branched systems (isobutane, isobutanol, *t*-butanol, and 2-butanol) and the systems lacking C–C bonds (methane and methanol) both exhibit *d*-wave behavior there. Although there is, to be sure, a degree of arbitrariness in classifying 2-butanol as a "branched"

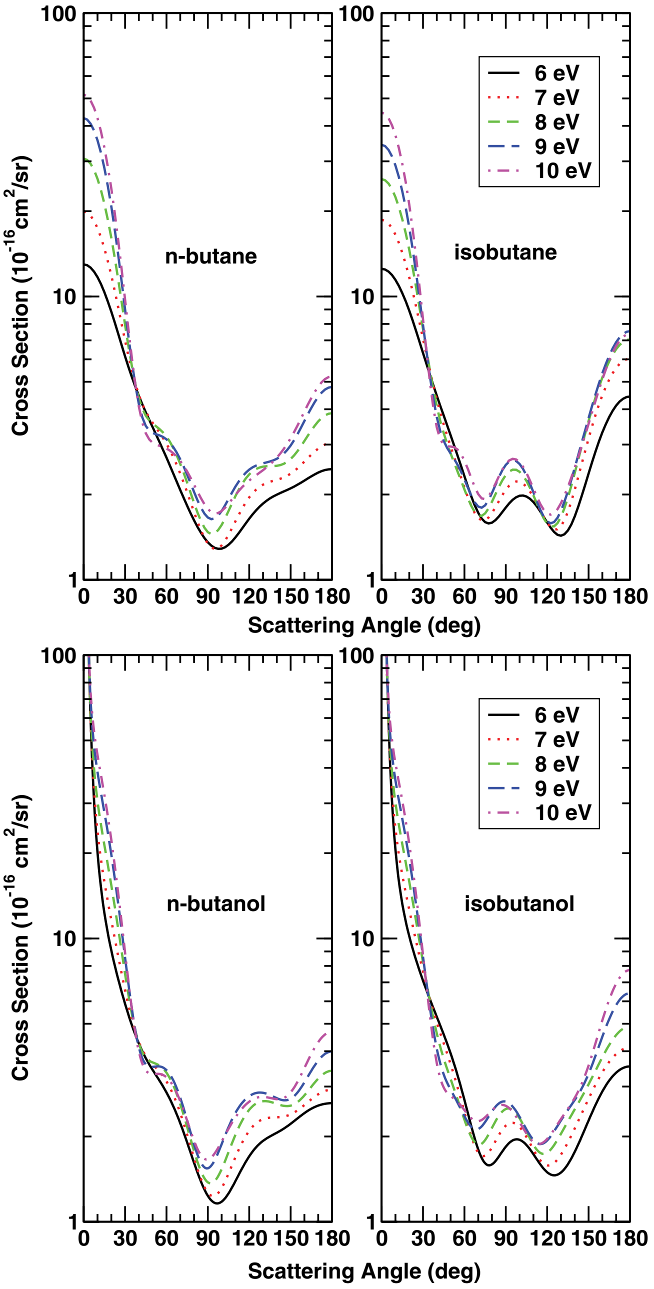

FIG. 5. (Color online) Differential cross sections for the C_4H_{10} isomers *n*-butane and isobutane and for the C_4H_9OH isomers *n*-butanol and isobutanol at 6, 7, 8, 9, and 10 eV. See text for discussion.

system due to its having both CH_3 and OH groups attached to carbon 2, while at the same time classifying methanol separately from the isoelectronic ethane, the overall trend is nonetheless suggestive.

Additional information comes from elastic electron scattering by structural and conformational isomers of the alkene butene, C_4H_8, which was studied by Lopes and co-workers [16]. Because the calculations of Lopes *et al.* omitted polarization effects and therefore are expected to place resonances too high in energy, the best comparison is probably to their differential cross sections at 10 eV. There the branched form, isobutene, exhibits a clear *d*-wave pattern, fitting the trend outlined in the preceding paragraph, and likewise, three straight-chain isomers, *trans*-2-butene, *anti*-1-butene [17], and *syn*-1-butene, show more or less an *f*-type pattern. A *d*-type pattern is seen in the remaining straight-chain isomer studied, *cis*-2-butene, indicating that the association of an unbranched backbone with *f*-wave scattering, though strong, is not universal.

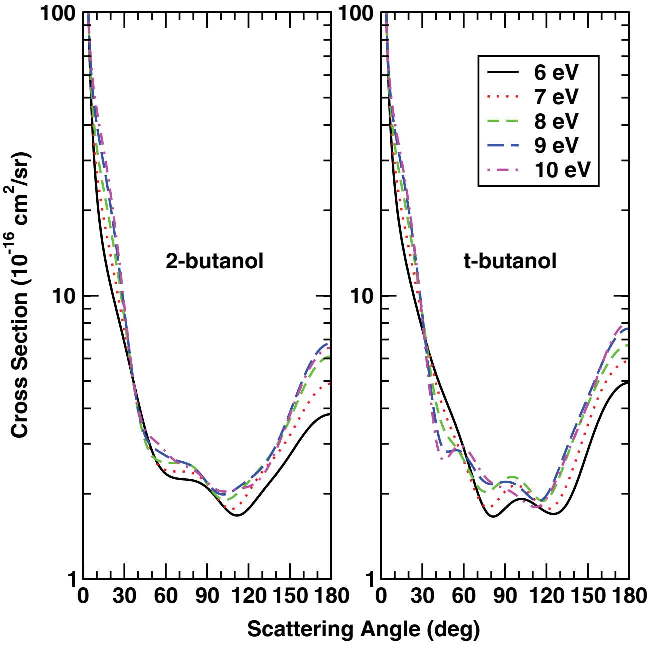

FIG. 6. (Color online) Differential cross sections for the C_4H_9OH isomers 2-butanol and *t*-butanol at 6, 7, 8, 9, and 10 eV. See text for discussion.

All of the molecules under discussion exhibit broad maxima in their integral elastic cross sections near 10 eV, which suggests that the appearance of the *d*- or *f*-wave scattering pattern at nearby energies is due to one or more short-lived shape resonances. As noted previously [4], the absence of *f*-wave behavior in methane and methanol may indicate that *f*-wave scattering arises from resonances (presumably σ^*) associated with C–C bonds, yet the dominance of *d*-wave scattering in the branched systems demonstrates that it is not just the types of bonds present but also their spatial arrangement that matters. Often it is possible to associate shape-resonant scattering with a particular unoccupied valence orbital of the target molecule. However, in the present case, examination of the canonical virtual orbitals did not prove informative; there are several closely spaced orbitals in the energy range of interest, and they are delocalized over the molecule and do not exhibit, at least to us, suggestive symmetry properties.

Two hypotheses that might explain the observed *d*- versus *f*-wave pattern appear plausible, although each has its limitations. First, the scattering pattern may be determined by the local symmetry of C–C antibonding orbitals that temporarily trap the projectile to form shape resonances; such localized orbitals would be linear combinations of the canonical orbitals. In a straight-chain system, a localized orbital centered on a given C–C bond might typically have a large f_{z^3} component about the bond axis, reflecting the contribution from out-of-phase carbon p orbitals directed along the bond. However, the local tetrahedral symmetry near the branching point in non-straight-chain systems could give rise to d-type linear combinations of C–C σ^* orbitals. The prototype here is CH_4, where the C–H bonding and antibonding orbitals form combinations that transform under the a_1 and t_2 representations of the T_d group, with d being the leading partial wave in t_2. Consistent with this picture, CH_4 is, as noted earlier, the only normal alkane to exhibit d-wave scattering. Even if this hypothesis is correct, however, it remains unclear why the C–C σ^* orbitals are more important than the C–H σ^* orbitals in determining the scattering pattern of, for instance, C_2H_6 or C_3H_8.

A second possibility is that the primary determinant of d- versus f-wave scattering is simply the spatial extent of the molecule. Branched systems are more compact than their corresponding straight-chain isomers, making it more difficult, at a given energy, for f waves to penetrate the angular-momentum barrier and reach the region of the molecular potential. Although this hypothesis makes sense within a family of isomers, it appears less plausible to us than the first because f-wave scattering is found in systems as small as C_2H_6, and conversely, d-wave scattering occurs in systems as large as t-butanol.

Further study of low-energy scattering by the alkanes and alkyl alcohols may help clarify the mechanism leading to the observed symmetry properties of the differential cross section. In particular, it would be informative to examine whether the cross section of isopropanol, in which the OH group is attached to the central carbon, behaves as a branched system with d-wave scattering or a straight-chain system with f-wave scattering.

IV. SUMMARY

We have presented integral, momentum-transfer, and differential cross sections for elastic collisions of low-energy electrons with the isomers of butanol, C_4H_9OH. The integral cross sections of the different isomers are similar to each other and to that of the straight-chain isomer n-butanol. However, between 5 and 10 eV, where broad shape resonances influence the scattering, the differential cross sections exhibit distinctive scattering patterns, with d-wave scattering predominating in the branched isomers while f-wave scattering is found in n-butanol. The present results generalize and extend previous results for other alcohols and for alkanes, where related resonant scattering patterns are found.

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[17] This species is labeled skew-1-butene in Ref. [16], but from its stated C_s symmetry and depiction in Fig. 1(e) of Ref. [16] it is clearly the *anti* conformer.