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We present a joint theoretical-experimental study on electron scattering by methanol (CH_3OH) and ethanol (C_2H_5OH) in a wide energy range. Experimental differential, integral and momentum-transfer cross sections for elastic electron scattering by ethanol are reported in the 100–1000 eV energy range. The experimental angular distributions of the energy-selected electrons are measured and converted to absolute cross sections using the relative flow technique. Moreover, elastic, total, and total absorption cross sections for both alcohols are calculated in the 1–500 eV energy range. A complex optical potential is used to represent the dynamics of the electron-alcohol interaction, whereas the scattering equations are solved iteratively using the Padé's approximant technique. Our calculated data agree well with those obtained using the Schwinger multichannel method at energies up to 20 eV. Discrepancies at high energies indicate the importance of absorption effects, included in our calculations. In general, the comparison between our theoretical and experimental results, as well as with other experimental data available in the literature, also show good agreement. Nevertheless, the discrepancy between the theoretical and experimental total cross sections at low incident energies suggests that the experimental cross sections measured using the transmission technique for polar targets should be reviewed. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3695211]

I. INTRODUCTION

Electron scattering by small alcohol molecules is a subject of current interest due to the use of these species as renewable energy sources replacing the traditional fossil fuels. Such uses would lead to an increase in the concentration of the vapors of small alcohols in the atmosphere in near future. Therefore, the investigation on electron-alcohol interaction may help on the understanding of energy and material balances in combustion plasmas, in the chemistry of such species in terrestrial atmosphere. In addition, the discovery of small alcohols in interstellar space and in the atmosphere of planets in the solar system has also motivated recent studies on electron interaction with these systems.

Experimentally, electron-methanol interactions have been intensively investigated over the years. An extensive list of references for such studies was cited in recent works of Khakoo et al.[1] and Silva et al.[2] Specifically, various cross-section measurements for e^--methanol collisions can be summarized as follows. Earlier measurements of grand-total (elastic plus inelastic) cross sections (TCS) were reported by of Schmieder[3] and Sueoka et al.[4] and more recently by Szmytkowski and Krzysztofowicz[5] and Silva et al.[2] Absolute values of partial and total ionization cross sections (TICS) were reported by Srivastava et al.,[6] Durić et al.,[7] and Rejoub et al.[8] Also, differential cross sections (DCS) and integral cross sections (ICS) for elastic electron scattering by methanol were recently reported by Khakoo et al.[1] and by

Sugohara et al.[9] in the 1–100 eV and 100–1000 eV energy ranges, respectively.

Theoretical investigations on electron-methanol collisions are significantly less abundant. Calculated DCS and ICS in the 1–100 eV range were reported by Khakoo et al.[1] using the Schwinger multichannel method (SMC) in the static-exchange (SE) and static-exchange-polarization (SEP) levels of approximation. Two different implementations of SMC, namely the all-electron (AE) version (which takes all electrons into account) and the pseudopotential (PP) version (which uses pseudopotentials to replace the core electrons and explicitly includes only the valence electrons), were used to perform the calculations. The ICS for elastic and electronic excitation processes up to 12 eV were also calculated by Bouchiha et al.[10] using the R-matrix method. At higher energies, ICS, TCS, and total absorption cross sections (TACS) calculated using the spherical complex optical potential approach (SCOP) and the group additivity rule (AR) were reported by Joshipura and Vinodkumar[11] and by Vinodkumar et al.[12] in the 15–5000 eV range. The DCS, ICS, and momentum-transfer cross sections (MTCS) were also calculated by Sugohara et al.[9] using the independent-atom model combined with the AR in the 100–1000 eV range.

Electron-ethanol collision studies, both theoretically and experimentally, are considerably scarcer. For this target, experimental TCS were reported by Schmieder[3] and Silva et al.[2] Experimental TICS were measured by Durić et al.[7]

and Rejoub *et al.*[8] Additionally, DCS and ICS were measured and calculated by Khakoo *et al.*[1] in the 1–100 eV range. The SMC AE and SMC PP approaches, in both SE and SEP levels of approximation, were used in their calculations.

Besides of electron-collision studies, some experimental investigations on positron interaction with small alcohols were recently performed as well. For instance, TCS for positron-methanol collisions were measured recently by Kimura *et al.*[13] in the 1–500 eV impact energy range and by Zecca *et al.*[14] in the 0.1–40 eV range. Experimental TCS for positron-ethanol collisions were also reported by Zecca *et al.*[14] in the 0.1–40 eV range. To know how electron and positron cross sections compare with one another may be a very interesting subject.

In this work, we report a joint theoretical-experimental investigation on elastic scattering of electrons by methanol and ethanol. Particularly, absolute experimental values of DCS, ICS, and MTCS in the 100–1000 eV energy range for ethanol are presented. Calculated DCS, ICS, MTCS, TCS, and TACS are also reported in the 1–500 eV energy range for both alcohols. Considering the scarceness of both theoretical and experimental results for e^--ethanol collisions, particularly at energies above 100 eV, the present study constitutes an attempt to partially fill this lack of data.

The organization of this paper is as follows: In Sec. II, we present some details of our experimental procedure. In Sec. III, details of the calculations are briefly described. In Sec. IV our measured results are compared with the present calculated results and with existing experimental and theoretical data. Some conclusive remarks are also summarized in Sec. V.

II. EXPERIMENTAL PROCEDURE

Details of our experimental setup and procedure can be found in our previous works[15, 16] and will only be briefly described here. Basically, for a given energy, the angular distribution of the energy-filtered electrons elastically scattered by the target is measured. A crossed electron beam-molecular beam geometry is used for this purpose. The energy of the scattered electrons is selected by using a retarding-field analyser with a resolution of about 1.5 eV. This resolution is sufficient to distinguish inelastically scattered electrons resulted from electronic excitation, but not for vibrational excitation processes. In our previous work,[17] we noted that vibrational excitation cross sections are negligible at energies above 100 eV, and thus do not affect our elastic experimental DCS for ethanol.

The measured electron intensity is converted to absolute DCS ($\frac{d\sigma}{d\theta}$) by using the relative-flow technique (RFT),[18, 19] as follows:

$$\left(\frac{d\sigma}{d\theta}\right)_x = \left(\frac{d\sigma}{d\theta}\right)_{std} \frac{I_x}{I_{std}} \frac{R_{std}}{R_x} \left(\frac{M_{std}}{M_x}\right)^{\frac{1}{2}}, \qquad (1)$$

where I is the scattered electron intensity, R is the relative-flow rate, and M is the molecular weight. The subscripts x and *std* refer to the gas under determination and the secondary standard, respectively. The application of RFT requires precise measurements of R for both gases, x and *std*. At room

temperature and under atmospheric pressure, ethanol is a liquid. Due to the polar nature of this alcohol, dimers of this species may be formed from its vapor. It is also possible that the injected vapors are adsorbed on the inner surfaces of the gas manifold. Both processes may lead to errors in the precise determination of R and consequently in the absolute calibration of the DCS. In order to prevent such errors, we have recently developed a systematic procedure[20] for accurate relative-flow-rate determination of gases and vapors. The method reported in that study has already been applied to evaluate the influence of the adsorption effects in the cross-section determination of methanol,[9] and it is also applied here for ethanol. As in the case of methanol, our study shows that the dimer formation of ethanol is negligible under the used experimental conditions.

In our absolute calibration of DCS, Ar and N_2 are used as secondary standards. Absolute DCS of Ar measured by Jansen *et al.*[21] in the 200–1000 eV energy range and those of N_2 of Dubois and Rudd[22] at 100 eV energy are used to normalize our data. Moreover, the ICS and MTCS are derived from the experimental DCS via numerical integrations.

Details of the analysis of experimental uncertainties have been given elsewhere.[16] The overall experimental uncertainties of 17% at 100 eV and 11% at 200 eV and above in our absolute DCS are estimated from the experimental conditions and from the quoted errors of the absolute DCS of Ar and N_2 found in the literature.[21, 22] The absolute DCS were determined in the 5°–130° angular range. In order to obtain ICS and MTCS, an extrapolation procedure was adopted to estimate DCS at scattering angles out of the angular range covered experimentally. The extrapolation was carried out manually. The overall uncertainties on ICS and MTCS are estimated to be 25% at 100 eV and 23% elsewhere.

III. THEORY

In the present study, the dynamics of electron-target interaction is described by a complex optical potential given by

$$V_{opt} = V_{st} + V_{ex} + V_{cp} + i V_{ab}, \qquad (2)$$

where V_{st} and V_{ex} are the static and the exchange components, respectively, and V_{cp} is the correlation-polarization contribution. In addition, V_{ab} is an absorption potential which is responsible for the reduction of the flux of elastically scattered electrons due to the opening of inelastic scattering channels. Using this optical potential, the scattering problem is solved exactly using the numerical solution of the Lippmann-Schwinger (LS) integral equation within the single-center-expansion close-coupling framework and further corrected using the Padé's approximant technique.[23] In recent past, this method was successfully applied by our group to treat electron collisions with ethane and propane.[24, 25] In this work, we extend its application to polar targets. The details of this method were already given elsewhere[23–25] and thus will only be outlined here.

Using an effective potential, the many-body nature of the electron-molecule interaction is reduced to a one-particle single-channel scattering problem. The corresponding

transition T matrix is given as

$$T_{fi} = \langle \phi(\vec{k}_f)|U_{opt}|\psi^+(\vec{k}_i)\rangle, \qquad (3)$$

where $U_{opt} = 2V_{opt}$ is the reduced optical potential, ϕ is the unperturbed plane wave function, and k is the magnitude of the electron linear momentum. Using a two-potential formalism we write

$$U_{opt} = U_1 + U_2, \qquad (4)$$

with

$$U_1 = U_{st} + U_{ex}^{loc} + U_{cp}, \qquad (5)$$

$$U_2 = U_{ex} - U_{ex}^{loc} + iU_{ab}, \qquad (6)$$

where U_{ex}^{loc} is a reduced local exchange potential. Hence, the T matrix can be rewritten as a sum of two parts

$$T_{fi} = T_1 + T_2, \qquad (7)$$

where

$$T_1 = \langle \phi(\vec{k}_f)|U_1|\psi_1^+(\vec{k}_i)\rangle, \qquad (8)$$

$$T_2 = \langle \psi_1^-(\vec{k}_f)|U_2|\psi^+(\vec{k}_i)\rangle. \qquad (9)$$

In Eqs. (8) and (9), ψ_1 is the solution of the LS equation with potential U_1. Further, T_2 can be obtained using the [N/N] Padé's approximant technique[23]

$$T_2[N/N] = -\sum_{i,j=1,N-1} \langle \psi_1^-|U_2|\phi^{(i)+}\rangle (D^{-1})_{ij} \langle \phi^{(j)-}|U_2|\psi_1^+\rangle,$$

$$(10)$$

where

$$D_{ij} = \langle \phi^{(i)-}|U_2 - U_2 G_1^+ U_2|\phi^{(j)+}\rangle, \qquad (11)$$

$$\phi^{(i)} = (G_1^+ U_2)^i \psi_1, \qquad (12)$$

with $\phi^{(0)} = \psi_1$. G_1 is the distorted-wave Green's function, which satisfies the following condition:

$$(\nabla^2 + k^2 - U_1)G_1^\pm(\vec{r}, \vec{r}') = \delta(\vec{r}, \vec{r}'). \qquad (13)$$

The superscripts $-$ and $+$ appearing in the above equations denote the incoming- and outgoing-boundary conditions of the scattering waves, respectively.

In the present work, U_{st} and U_{ex} are derived exactly from a near-Hartree-Fock self-consistent-field (SCF) target wave function, whereas U_{cp} is obtained in the framework of the free-electron-gas model, derived from a parameter-free local density, as prescribed by Padial and Norcross.[26] The dipole polarizabilities (in atomic units) $\alpha_{xx} = 18.89$, $\alpha_{yy} = 20.98$, $\alpha_{zz} = 18.11$, and $\alpha_{xy} = -0.65$ for methanol, and $\alpha_{xx} = 33.65$, $\alpha_{yy} = 30.49$, $\alpha_{zz} = 28.31$, and $\alpha_{xy} = -0.83$ for ethanol are used to generate the asymptotic form of U_{cp}. These values, calculated within the Hartree-Fock (HF) framework using a aug-cc-pVDZ basis, were taken from the website of NIST.[27] The potential U_{ab} in Eq. (6) is the reduced scaled quasi-free scattering model (SQFSM) absorption potential of Lee *et al.*[28] which is an improvement of the version 3 of the model absorption potential originally proposed by Staszewska *et al.*[29]

The Hara free-electron-gas-exchange potential[30] was used to generate the local exchange potential U_{ex}^{loc}.

Moreover, the TCS for electron-molecule scattering are obtained using the optical theorem

$$\sigma_{tot} = \frac{4\pi}{k} Im(f(\theta = 0°)). \qquad (14)$$

The wave functions of the ground states of methanol and ethanol, used in the generation of e^--target potential, were calculated at the HF SCF level. The calculations were performed using the quantum chemistry code GAMESS [31] with an aug-cc-pVDZ contracted Gaussian basis set. The optimized equilibrium geometries of the alcohols, also taken from the same website of NIST,[27] were used for this purpose.

In our calculation, the wave functions, the interaction potentials, and the related matrices are partial-wave expanded around the center-of-mass of the molecule. The truncation parameters used in these expansions are: $l_c = 25$ and $h_c = 25$ for all bound and continuum orbitals and for the T-matrix elements. The calculated cross sections were converged within 6 iterations, that is $N = 7$ in Eq. (10).

Since methanol and ethanol are polar systems with experimental dipole moments of 1.70 D and 1.69 D,[32] respectively, the partial-wave expansions converge slowly due to the long-range nature of the dipole interaction potential. In order to overcome this difficulty, a Born-closure formula is used to account for the contribution of higher partial-wave components to the scattering amplitudes. The procedure used is the same as in some of our previous studies.[33,34]

IV. RESULTS AND DISCUSSION

A. Methanol

Experimental data of DCS, ICS, and MTCS for elastic electron scattering by methanol in the 100–1000 eV energy range were recently published by our group.[9]

In Fig. 1, we present our calculated DCS for this target at incident energies of 5, 10, 50, and 500 eV. Our previous experimental results, as well as the calculated and measured data of Khakoo *et al.*[1] are also shown for comparison. The theoretical DCS of Khakoo *et al.* were obtained using the Schwinger multichannel method, both in the SMC AE and SMC PP versions, at the SEP level of approximation. Therefore, no absorption effects were taken into account in their calculations. At low incident energies (here at 5 eV and 10 eV), where the absorption effects are negligible, all the calculated results agree well with each other. The agreement between the calculated results and experimental data is also good, except at 5 eV where the experimental hump around 90° is not reproduced in the calculations. At higher energies, the absorption effects become relevant. For instance, at 50 eV, our theoretical results calculated with the inclusion of such effects agree well with the existing experimental data,[1] whereas the theoretical data calculated using the SMC[1] without absorption significantly overestimate the experimental data. Moreover, at 500 eV, our calculations still agree well with the experimental DCS,[9] although some unphysical oscillations are seen near the backward region. These oscillations are due to the poor
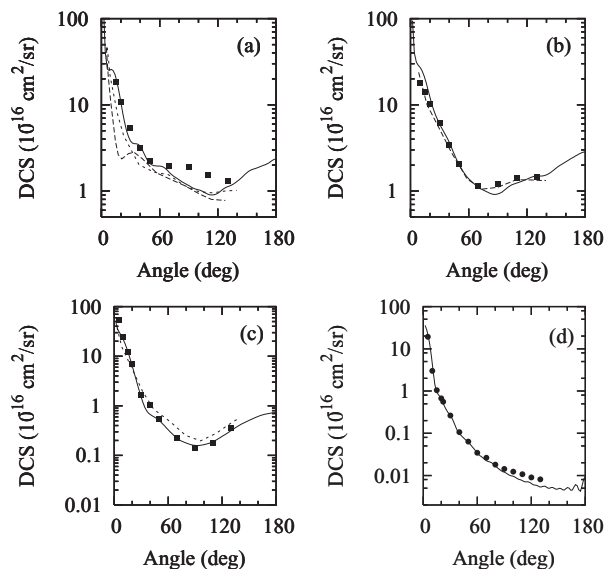
FIG. 1. DCS for elastic electron scattering by methanol at (a) 5 eV, (b) 10 eV, (c) 50 eV, and (d) 500 eV. Solid line, present theoretical results; dashed line, calculated results of Khakoo *et al.*[1] using the SMC AE; short-dashed line, calculated results of Khakoo *et al.* using the SMC PP; solid squares, measured results of Khakoo *et al.*,[1] solid circles, experimental data of Sugohara *et al.*[9]

convergence of the partial-wave expansion at the higher end of incident energies.

In Figs. 2(a)–2(d), we show our calculated ICS, MTCS, TCS, and TACS for electron scattering by methanol in the 1–500 eV energy range. In Fig. 2(a), we compare our data with
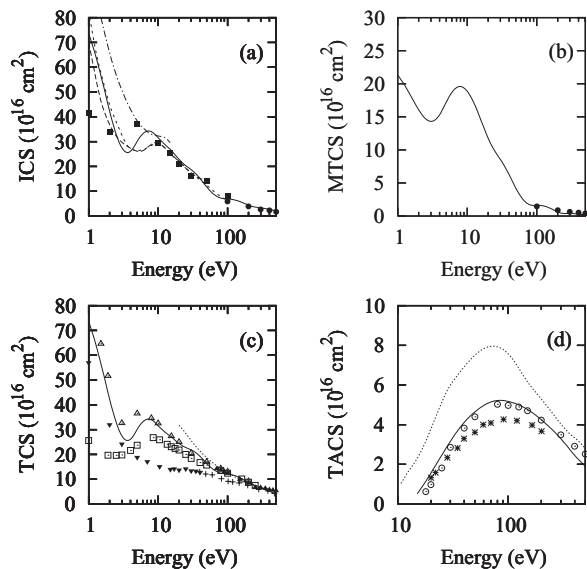

FIG. 2. (a) ICS, (b) MTCS, (c) TCS, and (d) TACS for electron-methanol collisions. Solid line present theoretical results; dashed line, calculated results of Khakoo *et al.*[1] using the SMC AE; short-dashed line, calculated results of Khakoo *et al.* using the SMC PP; dashed-dotted line, calculated ICS of Bouchiha *et al.*;[10] (c) dotted line, present theoretical TCS of Vinodkumar *et al.*;[12] (d) dotted line, theoretical TACS of Joshipura and Vinodkumar;[11] (a) solid squares, measured results of Khakoo *et al.*;[1] (b) solid circles, experimental data of Sugohara *et al.*;[9] (c) open squares, experimental TCS of Szmytkowski and Krzysztofowicz,[5] open triangles, corrected experimental TCS of Szmytkowski and Krzysztofowicz (see text), inverted triangles, experimental TCS of Zecca *et al.*,[14] and crosses, experimental TCS of Kimura *et al.*,[13] both for positron-methanol collision; (d) asterisks, experimental TICS of Durić *et al.*;[7] open circles, experimental TICS of Rejoub *et al.*[8]
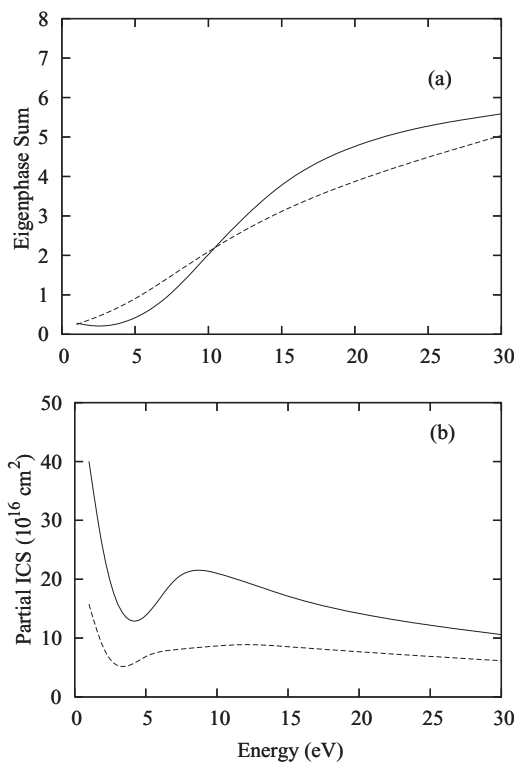

FIG. 3. (a) Eigenphase sums and (b) partial ICS for electron-methanol collisions in the 1–30 eV energy range. Solid line, present theoretical results for the *A'* symmetry; dashed line, calculated results for the *A"* symmetry.

the experimental ICS of Khakoo *et al.*[1] and Sugohara *et al.*[9] Comparison is also made with the theoretical ICS of Khakoo *et al.* calculated using both the SMC AE and SMC PP approaches, and with the theoretical ICS of Bouchiha *et al.* using the R-matrix method.[10] Qualitatively, our calculated ICS, (as well as MTCS and TCS) show an enhancement centered at about 8 eV, with width of approximately 6 eV. A similar feature was also seen in the ICS calculated with both SMC implementations and in the R-matrix ICS,[10] although the latter is shifted towards higher incident energies. In order to understand the physical origin of these structures, the eigenphase sums and partial ICS calculated for both *A'* and *A"* scattering symmetries in the 1–30 eV range are presented in Figs. 3(a) and 3(b), respectively. The eigenphase-sum analysis indicates that the enhancement in our calculated ICS can in fact be associated to shape resonances in these scattering channels. In addition, a broad maximum centered around 8 eV in the partial ICS of the *A'* channel also reinforces this conclusion, although there is no clear indication of the existence of a maximum in the partial ICS of the *A"* channel. However, the increase of almost 2π in the eigenphase sums may indicate a possible occurrence of two, rather than just one, resonances of each scattering symmetry in this energy range. As pointed out by Khakoo *et al.*,[1] the resonance feature seen in the ICS does not show any evidence to be associated with the low-energy OH $\sigma*$ shape resonance which gives rise to a peak near 3 eV in the dissociative attachment cross section as postulated by Ibãnescu *et al.*[35] There is also no evidence to associate it with the attachment peaks seen near 6.5, 8, and 10 eV in that study.[35] This conclusion can also be extracted from the width of about 6 eV of the calculated resonances. The associated

lifetime of the compound state is about 10^{-16} s, too short for the formation of the negative fragments reported by Ibãnescu *et al.*[35] In fact, the fragments at about 10 eV in their study are assigned to electronic Feshbach resonances, which can not be predicted in the present study since no multichannel coupling is explicitly accounted for in our calculations.

Quantitatively, the R-matrix ICS calculated with dipole-Born correction lie significantly above our data at energies up to 8 eV. As pointed out by Khakoo *et al.*,[1] the dipole-Born correction made by Bouchiha *et al.* was not on the scattering amplitudes but directly on the cross sections, which may result in the observed discrepancies. Moreover, our results also agree well with both experimental results, except near 1 eV, where all calculations lie well above the experimental data of Khakoo *et al.* Possibly, such discrepancies are due to the uncertainty in the extrapolation of their experimental DCS towards the forward direction. At low incident energies their experimental DCS were measured in the $20°$–$140°$ angular range. The DCS near the forward direction are strongly peaked due to the polar nature of methanol and therefore contribute dominantly to the ICS.

In Fig. 2(b), our calculated MTCS are compared with the experimental data of Sugohara *et al.*[9] in the 100–500 eV range. There is a very good agreement between the calculated and experimental data. Unfortunately for this target, no other experimental or theoretical MTCS, particularly at lower energies, are available to be compared with our data.

In Fig. 2(c), our calculated TCS are compared with the experimental results of Szmytkowski and Krzysztofowicz[5] in the 1–250 eV energy range and those of Silva *et al.*[2] in the 60–500 eV energy range. The experimental TCS of Schmieder[3] and Sueoka *et al.*[4] are essentially similar to those of Szmytkowski and Krzysztofowicz, and therefore are not shown. The calculated TCS of Vinodkumar *et al.*[12] using the

SCOP is also shown in the 15–500 eV range for comparison. At 30 eV and above, our calculated TCS agree very well with both experimental data.[2,5] The calculated TCS of Vinodkumar *et al.*[12] also agree with our data at energies above 50 eV. Nevertheless, our calculated data significantly overestimate the experimental TCS of Szmytkowski and Krzysztofowicz[5] at energies below 15 eV. It is also interesting to note that their measured TCS are even smaller than the experimental ICS of Khakoo *et al.*[1] at energies up to 10 eV, which is inconsistent since the ICS account only for the contribution of the elastic scattering channel. Moreover, the similarity of the existing experimental TCS in this energy range for methanol[3–5] seems to indicate the occurrence of a systematic error in the TCS measured using the transmission technique for polar targets. As pointed out by Bouchiha *et al.*,[10] similar discrepancies were also observed in the TCS of other polar targets as H_2O. A possible explanation for this fact is that the electron transmission experiments are unable to distinguish the transmitted electrons from those elastically scattered at very small angles. For polar molecules, the strongly peaked DCS near the forward direction may lead to an underestimation of TCS. The acceptance angle of the detector reported in the experimental setup of Szmytkowski and Krzysztofowicz[5] is 0.7 msr, which corresponds to an angular range of $0°$–$1.7°$. In order to estimate the possible loss of TCS due to this problem, we performed a numerical integration of our calculated DCS over this angular range. The resulting ICS are added to the TCS reported by Szmytkowski and Krzysztofowicz.[5] The so corrected TCS is also plotted in Fig. 2(c) for comparison. It is seen that there is a very good agreement between our calculated and the corrected experimental TCS. This good agreement seems to indicate that the TCS measured using the transmission technique for polar targets at low incident energies are significantly underestimated.

TABLE I. Experimental DCS (in 10^{-16} cm^2/sr), ICS, and MTCS (in 10^{-16} cm^2) for elastic e^--ethanol scattering.

| Angle (deg)	E_0 (eV)					
	100	200	300	400	500	1000
5	4.67(1)[a]	2.38(1)	1.64(1)	2.76(1)	1.26(1)	1.68(1)
10	2.20(1)	1.27(1)	7.24(0)	5.77(0)	4.15(0)	3.33(0)
15	7.60(0)	3.85(0)	2.70(0)	2.19(0)	2.23(0)	1.35(0)
20	2.76(0)	1.66(0)	1.64(0)	1.22(0)	1.18(0)	7.81(−1)
25	1.55(0)	1.14(0)	9.30(−1)	6.88(−1)	7.60(−1)	3.29(−1)
30	9.87(−1)	7.49(−1)	5.91(−1)	4.63(−1)	4.82(−1)	1.84(−1)
40	5.45(−1)	3.54(−1)	2.91(−1)	1.66(−1)	1.59(−1)	7.36(−2)
50	3.09(−1)	1.65(−1)	1.21(−1)	9.38(−2)	9.31(−2)	3.41(−2)
60	2.14(−1)	8.15(−2)	8.95(−2)	6.13(−2)	4.89(−2)	1.88(−2)
70	1.24(−1)	7.01(−2)	6.91(−2)	3.58(−2)	3.68(−2)	1.28(−2)
80	8.25(−2)	5.44(−2)	4.36(−2)	2.88(−2)	2.75(−2)	7.29(−3)
90	7.42(−2)	4.87(−2)	3.69(−2)	2.37(−2)	2.08(−2)	5.72(−3)
100	1.14(−1)	5.09(−2)	3.56(−2)	1.79(−2)	1.73(−2)	4.48(−3)
110	1.37(−1)	4.76(−2)	3.14(−2)	1.75(−2)	1.37(−2)	3.81(−3)
120	1.65(−1)	5.20(−2)	3.20(−2)	1.73(−2)	1.32(−2)	3.30(−3)
130	1.83(−1)	5.59(−2)	3.18(−2)	1.79(−2)	1.30(−2)	2.88(−3)
ICS	9.06(0)	5.08(0)	3.70(0)	3.11(0)	2.57(0)	1.92(0)
MTCS	2.48(0)	9.34(−1)	6.35(−1)	3.90(−1)	3.42(−1)	1.21(−1)

[a]4.67(1) means 4.67×10^1.
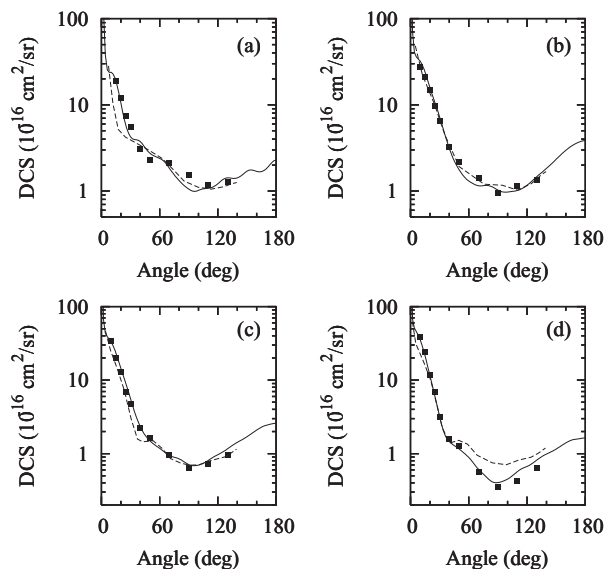
FIG. 4. DCS for elastic electron scattering by ethanol at (a) 5 eV, (b) 15 eV, (c) 20 eV, and (d) 30 eV. Solid line, present theoretical results; dashed line, calculated results of Khakoo *et al.*[1] using the SMC AE; solid squares, measured results of Khakoo *et al.*[1]
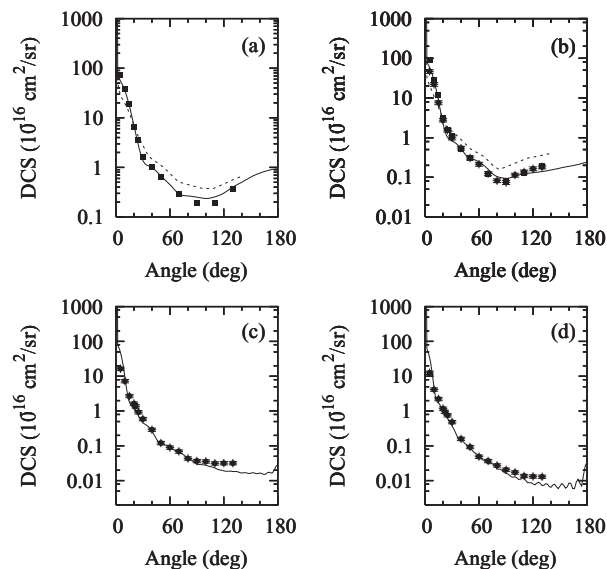
FIG. 5. Same as in Fig. 4 but for (a) 50 eV, (b) 100 eV, (c) 300 eV, and (d) 500 eV. The symbols are the same as in Fig. 4, except: solid circles, present experimental data; short-dashed line, calculated results of Khakoo *et al.* using the SMC PP.

In Fig. 2(d), we compare our calculated TACS with the experimental TICS of Durić *et al.* [7] and Rejoub *et al.*[8] The calculated TACS of Joshipura and Vinodkumar[11] using the SCOP are shown as well. It is well known that at energies above 100 eV, the ionization process dominates the inelastic electron-molecule interactions.[36] Therefore, it is expected that the comparison between our TACS and the experimental TICS is meaningful. In general, our calculated TACS agree well with both experimental data. The TACS of Joshipura and Vinodkumar[11] agree qualitatively with our data, although they are significantly overestimated.

B. Ethanol

Experimental DCS, ICS, and MTCS for elastic electron scattering by ethanol are presented in Table I for energies ranging from 100 eV to 1000 eV.

In Figs. 4 and 5 we show our calculated DCS for this target in the 5–500 eV energy range along with the present experimental results, as well as the calculated and measured data of Khakoo *et al.*[1] In Figs. 6(a)–6(d), our calculated ICS, MTCS, TCS, and TACS for electron scattering by ethanol are compared with the present measured and existing theoretical[1] and experimental results [1–3,7,8] in the 1–500 eV energy range.

In general, the present experimental DCS agree well with those of Khakoo *et al.* at the only overlapping energy of 100 eV. For this target, most comments made on e^--methanol collision are also pertinent. For instance, our calculated DCS agree well with the present experimental data and those of Khakoo *et al.*[1] Our calculated data also agree well with the theoretical DCS of Khakoo *et al.* at low incident energies, but not so well at 30 eV and above, where the absorption effects become relevant. Also, the structure in our calculated ICS, MTCS, and TCS at around 10 eV (see Fig. 6) is due to the occurrence of shape resonances in both the A' and A''

scattering channels. The agreement between our calculated ICS, MTCS, TCS, and TACS with the present experimental data and with the existing theoretical and measured results are also good, reflecting the reliability of the method used in the present study. It is interesting to note that near the lower-end of incident energies, the values of the calculated ICS and TCS for methanol and ethanol are very similar to each other. This is due to the fact that the dipole moments of methanol and
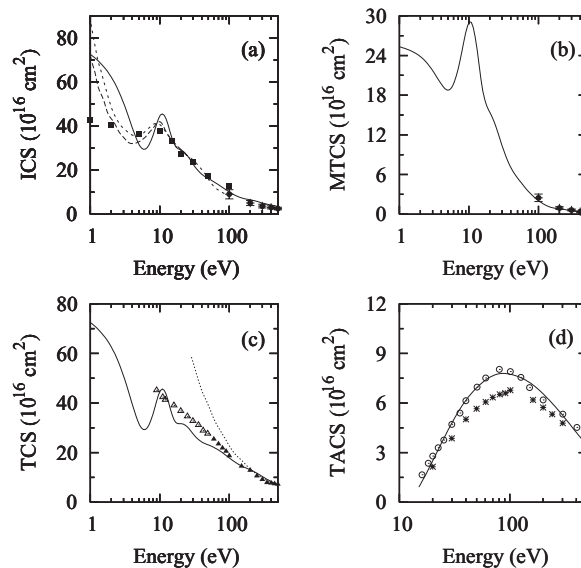

FIG. 6. (a) ICS, (b) MTCS, (c) TCS, and (d) TACS for electron-ethanol collisions. Solid line, present theoretical results; dashed line, calculated results of Khakoo *et al.*[1] using the SMC AE; short-dashed line, calculated results of Khakoo *et al.* using the SMC PP; dotted line, theoretical TCS of Silva *et al.*[2] using the AR; solid squares, measured results of Khakoo *et al.*,[1] solid circles, present experimental data; open triangles, experimental TCS of Schmieder;[3] asterisks, experimental TICS of Durić *et al.*;[7] open circles, experimental TICS of Rejoub *et al.*[8]

ethanol are about the same, and at very low incident energies, the scattering dynamics is dominated by dipole interactions.

V. CONCLUSIONS

In this work, we report a joint theoretical-experimental investigation on electron scattering by methanol and ethanol in a wide energy range. Experimentally, DCS, ICS, and MTCS for elastic electron scattering by ethanol are measured in the 100–1000 eV energy range using the RFT. At the only overlapping energy, our measured results are in good agreement with the previous study of Khakoo *et al.*[1] Moreover, our calculated cross sections for both alcohols agree very well with the present and existing experimental results and with those calculated by Khakoo *et al.*[1] at the same level of approximation. Nevertheless, they diverge at higher energies, where absorption effects become relevant.

For both alcohols, a broad maximum structure is seen in the calculated ICS, MTCS, and TCS. This maximum is identified as shape resonances in both the A' and A'' scattering symmetries. However, there is no evidence that associates them to the negative fragments observed by Ibãnescu *et al.*[35]

At energies below 15 eV, our theoretical TCS for methanol disagree strongly with the existing experimental data.[3–5] This discrepancy is probably originated from the indistinguishability between the transmitted electrons and those elastically scattered near the forward direction. A numerical integration of our theoretical DCS over the experimental acceptance angle of Szmytkowski and Krzysztofowicz[5] is performed and the resulting values are used to correct their experimental TCS. A very good agreement between the calculated TCS and the so corrected experimental TCS is seen over the entire energy range. This fact suggests that the experimental TCS for polar targets, measured using the transmission technique, should be reviewed.

[1]M. A. Khakoo, J. Blumer, K. Keane, C. Campbell, H. Silva, M. C. A. Lopes, C. Winstead, V. McKoy, R. F. da Costa, L. G. Ferreira, M. A. P. Lima, and M. H. F. Bettega, Phys. Rev. A **77**, 042705 (2008).
[2]D. G. M. Silva, T. Tejo, J. Muse, D. Romero, M. A. Khakoo, and M. C. A. Lopes, J. Phys. B **43**, 015201 (2010).
[3]F. Schmieder, Z. Elektrochem. Angew. Phys. Chem. **36**, 700 (1930).
[4]S. Mori, Y. Katayama, and O. Sueoka, At. Coll. Res. Jpn. Prog. Rep. **11**, 19 (1985).
[5]C. Szmytkowski and A. M. Krzysztofowicz, J. Phys. B **28**, 4191 (1995).
[6]S. K. Srivastava, E. Krishnakumar, A. F. Fucaloro, and T. van Note, J. Geophys. Res. **101**, 26155, doi:10.1029/96JE02471 (1996).
[7]N. Durić, I. Cadez, and M. Kurepa, Fizika (Zagreb) **21**, 339 (1989).
[8]R. Rejoub, C. D. Morton, B. G. Lindsay, and R. F. Stebbings, J. Chem. Phys. **118**, 1756 (2003).
[9]R. T. Sugohara, M. G. P. Homem, I. P. Sanches, A. F. de Moura, M. T. Lee, and I. Iga, Phys. Rev. A **83**, 032708 (2011).
[10]D. Bouchiha, J. D. Gorfinkiel, L. G. Caron, and L. Sanche, J. Phys. B **40**, 1259 (2007).
[11]K. N. Joshipura and M. Vinodkumar, Eur. Phys. J. D **5**, 229 (1999).
[12]M. Vinodkumar, C. Limbachiya, K. N. Joshipura, B. Vaishnav, and S. Gangopadhyay, J. Phys.: Conf. Ser. **115**, 012013 (2008).
[13]M. Kimura, O. Sueoka, A. Hamada, and Y. Itikawa, Adv. Chem. Phys. **111**, 537 (2000).
[14]A. Zecca, L. Chiari, A. Sarkar, K. L. Nixon, and M. J. Brunger, Phys. Rev. A **78**, 022703 (2008).
[15]I. Iga, M. T. Lee, M. G. P. Homem, L. E. Machado, and L. M. Brescansin, Phys. Rev. A **61**, 227081 (2000).
[16]P. Rawat, I. Iga, M. T. Lee, L. M. Brescansin, L. E. Machado, and M. G. P. Homem, Phys. Rev. A **68**, 052711 (2003).
[17]M. G. P. Homem, R. T. Sugohara, I. P. Sanches, M. T. Lee, and I. Iga, Phys. Rev. A **80**, 032705 (2009).
[18]S. K. Srivastava, A. Chutjian, and S. Trajmar, J. Chem. Phys. **63**, 2659 (1975).
[19]J. C. Nickel, P. W. Zetner, G. Shen, and S. Trajmar, J. Phys. E: J. Sci. Instrum. **22**, 730 (1989).
[20]M. G. P. Homem, I. Iga, R. T. Sugohara, I. P. Sanches, and M. T. Lee, Rev. Sci. Instrum. **82**, 01319 (2011).
[21]R. H. J. Jansen, F. J. de Heer, H. J. Luyken, B. van Wingerden, and H. J. Blaauw, J. Phys. B **9**, 185 (1976).
[22]R. D. Dubois and M. E. Rudd, J. Phys. B **9**, 2657 (1976).
[23]F. A. Gianturco, R. R. Lucchese, and N. Sanna, J. Chem. Phys. **102**, 5743 (1995).
[24]P. Rawat, M. G. P. Homem, R. T. Sugohara, I. P. Sanches, I. Iga, G. L. C. de Souza, A. S. dos Santos, R. R. Lucchese, L. E. Machado, L. M. Brescansin, and M.-T. Lee, J. Phys. B **43**, 22502 (2010).
[25]G. L. C. de Souza, A. S. Santos, M.-T. Lee, L. E. Machado, L. M. Brescansin, R. R. Lucchese, R. T. Sugohara, I. P. Sanches, M. G. P. Homem, P. Rawat, and I. Iga, Phys. Rev. A **82**, 012709 (2010).
[26]N. T. Padial and D. W. Norcross, Phys. Rev. A **29**, 1742 (1984).
[27]Computational Chemistry Comparison and Benchmark Database - NIST, see http://cccbdb.nist.gov.
[28]M.-T. Lee, I. Iga, L. E. Machado, L. M. Brescansin, E. A. y Castro, I. P. Sanches, and G. L. C. de Souza, J. Electron Spectrosc. Relat. Phenom. **155**, 14 (2007).
[29]G. Staszewska, D. W. Schwenke, D. Thirumalai, and D. G. Truhlar, Phys. Rev. A **28**, 2740 (1983).
[30]S. Hara, J. Phys. Soc. Jpn. **22**, 710 (1967).
[31]M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, J. Comput. Chem. **14**, 1347 (1993).
[32]*Handbook of Chemistry and Physics*, 73rd ed., edited by David R. Lide (CRC Press, Boca Raton, 1992).
[33]M.-T. Lee, I. Iga, L. M. Brescansin, L. E. Machado, and F. B. C. Machado, Phys. Rev. A **66**, 012720 (2002).
[34]P. Rawat, I. Iga, M.-T. Lee, L. M. Brescansin, M. G. P. Homem, and L. E. Machado, Phys. Rev. A **68**, 052711 (2003).
[35]B. C. Ibãnescu, O. May, A. Monney, and M. Allan, Phys. Chem. Chem. Phys. **9**, 3163 (2007).
[36]K. N. Joshipura, M. Vinodkumar, and P. M. Patel, J. Phys. B **34**, 509 (2000).