

Electron scattering distributions as a probe of adsorbate orientation: CO and N₂

S. Nagano,^{a)} Z.-P. Luo, and H. Metiu

Department of Chemistry, University of California, Santa Barbara, California 93106

W. M. Huo

NASA-Ames Research Center, MS 230-3, Moffett Field, California 94035

V. McKoy

A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

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We calculate the differential cross section for elastic electron scattering by adsorbed CO and N₂. The dependence of this cross section on the azimuthal angle of detection depends on the molecular orientation and can be used to differentiate between a molecule lying flat on the surface, a tilted molecule, and an upright one. For molecules lying flat on the surface the orientation of the molecular axis and of the C and O atoms with respect to the plane of incidence of the electron can be determined.

I. INTRODUCTION

This article is part of a series^{1,2} investigating whether one can use the electron angular distribution generated by electron-adsorbate scattering experiments to obtain information about adsorbate orientation. Such experiments could be performed in many laboratories but wide use of such spectra has been hampered by the fear that they are more tedious than useful. Our intention is to use theory to assess this perception. Presently the complexity of electron-scattering calculations is such that one cannot hope to examine systems as complicated as adsorbed molecules without a significant number of simplifying assumptions. But even with such constraints the theory can precede the experiment in surveying the territory and mapping out the most advantageous strategy for experiment to follow. Even conclusions arrived at by less than perfect estimates are worth exploring experimentally, if they predict that different adsorbate structures will cause *massive* and *qualitative* changes in spectral *patterns*.

A sturdy and qualitatively reliable, but less quantitative, calculation can be used to answer important questions. For example, if we have some interest in adsorbed CO, can we tell, from the angular distribution of the electron, if it lies flat or is upright? A more ambitious question is: can we determine the tilt angle, if the molecule is tilted? If we want to answer such questions experimentally: which scattering channel gives more information readily: the elastic, the vibrationally inelastic, or the electronically inelastic? If the dipole selection rules imply a certain molecular orientation, should the conclusion be trusted under normal experimental conditions which are remote from the regime for which the rules are supposed to work?

The calculations presented here use a fairly reliable method³ for calculating the electron scattering amplitude by the adsorbed molecule. We cut corners in two respects: (a)

we neglect the fact that chemisorption modifies the electronic structure of the adsorbed molecule and (b) we use a distorted wave approximation and a flat surface to describe the way in which scattering by the metal contributes to the total scattering cross section. Briefly, we have modified the old Evans-Mills model⁴ to incorporate scattering by the molecule accurately, instead of using perturbation theory and assuming that the molecule is an oscillating point dipole. Moreover, we have modified the surface scattering amplitude to include the fact that not all the electrons reaching the surface are reflected.

The use of a flat surface within the distorted wave approximation can be first defended sociologically: it has been part of the Evans-Mills theory which is still the dominant and most useful tool in the field. More rational arguments are: (a) most experiments use electron beams with large de Broglie wave lengths and small coherence lengths, so that diffraction effects may be negligible; (b) some of the surface effects can be subtracted experimentally by comparing experiments performed with and without the adsorbate; (c) one can hope that the errors made by using a flat surface in the calculation will not *radically* alter the angular pattern.

The present theory can easily use potentials that mimic the local surface configuration. One can also use *T* matrices provided by LEED calculations, to examine how important it is to improve the manner in which the role of the surface is included in the model. Pursuing such improvements is worthwhile, and we are contemplating doing it. However, at this time we have accepted the fact that any theory of electron scattering by adsorbates must make some error, and we are trying to cope with this situation by lowering our expectations and by using the model only in situations in which changes in adsorbate structure cause *major* changes in scattering patterns.

In this article we examine near-specular scattering by CO and N₂ at an incident energy of 9.9 eV and an angle of incidence (with the surface normal) of 45°. We find that the azimuthal angular distribution of the scattered electrons can be used to differentiate between an upright molecule and one

^{a)} Present address: Fundamental Research Laboratory, NEC Corporation, Kawasaki, Kanagawa 213, Japan.

lying down. It is, however, not sufficiently sensitive to permit the determination of the angle of tilt with respect to the surface.

II. RESULTS

The number of parameters that can be varied in the present calculation is rather large. As a result we changed only those for which we expected reasonably large effects, namely (1) the position of the molecule with respect to the surface and the plane of incidence of the electron beam and (2) the azimuthal angle of detection. In all calculations the beam energy was 9.9 eV. We have used this value to avoid the well known low energy CO resonance.⁵ For chemisorbed CO this resonance is likely to be shifted below vacuum. If it is not, then the presence of the surface will broaden the resonance substantially because the electron in the temporary negative ion, which is responsible for the resonance, can jump into the empty states of the metal. A large jumping rate leads to a broad resonance; the disappearance of the electron into the sample (and then into the ground) will diminish the total intensity of the resonant signal. Since our model does not incorporate such effects it seems pointless to calculate the cross section in the energy range where the resonance might occur.

The polar angles of incidence and detection are chosen to be 45° with respect to the surface normal. Of course, we do not expect the experiments to be performed in the specular direction since the signal from the electrons scattered specularly by the surface will overwhelm the useful signal due to the scattering by the adsorbate. Since the dependence of the molecular cross section on the polar angle of detection is not dramatic the results are very similar for a 5° off-specular detection, for which such experiments are possible.

The scattering amplitudes for the e -CO and e -N₂ collisions used in these studies were obtained in the static-exchange approximation using the Schwinger multichannel formulation.³ In this approximation the electron is scattered by the nonlocal Hartree-Fock potential associated with the charge density of the molecular orbitals of the target molecule. No polarization of the molecular charge density by the incident electron is included. This approximation is known to work well at the energy of interest here. Details of these calculations, e.g., the Gaussian basis sets used in obtaining the static-exchange scattering amplitudes via the Schwinger variational method, are discussed elsewhere.^{6,7}

The distance between the molecule and the plane where the surface in our model reflects electrons was kept constant and equal to 1 Å. Changing this quantity by 0.25–0.5 Å does not alter substantially the scattering pattern.

The azimuthal detection angle was defined with respect to the plane of incidence as shown in Fig. 1.

A. Scattering by a CO molecule lying flat on the surface

In Fig. 2(a) we show the dependence of the electron scattering cross section $\sigma(\phi)$ on the azimuthal angle of detection ϕ , for a CO molecule lying flat on the surface. Both atoms are located at a height of 1 Å above the plane where in our model the electrons are reflected.

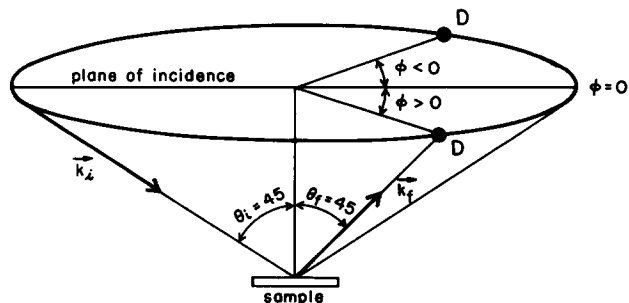


FIG. 1. The coordinate system used to describe the scattering process. The plane of the surface and the plane of incidence are used for reference. The polar angles θ_i and θ_f for the direction of incidence and that of detection, respectively, are defined with respect to the normal to the surface. In all calculations we kept $\theta_i = \theta_f = 45^\circ$. The azimuthal angle ϕ is zero if the detector is located in the specular direction. $\phi > 0$ when the detector is at the right-hand side of the plane of incidence. $\phi = +180 = -180$ for backward scattering.

The symmetric curve, marked with stars, shows $\sigma(\phi)$ for a CO molecule which is parallel to the plane of incidence of the electrons, with the oxygen end towards the electron gun. The electron flux dips in the forward direction, has maxima at 65° at the left and the right of the incident beam and gives no backward scattering. The curve marked with circles shows $\sigma(\phi)$ for the case when CO is parallel with the plane of incidence and the surface, and the C end is towards the electron gun. The angular dependence is symmetric around the forward direction and it is quite distinct from the case when the oxygen atom points towards the electron gun. The curve marked with crosses shows $\sigma(\phi)$ for a CO molecule which lies flat on the surface with its axis perpendicular to the plane of incidence. The O atom is at the left as seen from the electron gun position.

It is interesting to compare these results to those obtained in the absence of the surface by scattering electrons from a non-rotating molecule [Fig. 2(b)]. The patterns are very similar to those observed in the presence of the surface. This was not the case in our previous calculations for electronic excitation of H₂¹ where the presence of the surface affected the angular dependence of the cross section substantially.

B. Scattering by the N₂ molecule lying flat on the surface

The dependence of $\sigma(\phi)$ on ϕ for N₂ is very similar to that of CO except that both curves are now symmetric [Fig. 3(a)]. The scattering cross section for a nonrotating molecule in the absence of the surface [Fig. 3(b)] is almost identical to that obtained when the surface is present.

C. Scattering by standing and tilted CO

In Fig. 4(a) we show $\sigma(\phi)$, for CO standing on a surface, as a curve marked by circles. The molecule is perpendicular to the surface with the C end down and located 1 Å above the surface plane. In this case the scattering is peaked in the forward direction and has minima at $\pm 120^\circ$. The backward scattering intensity is 1/3 of the forward one. In the same figure we show $\sigma(\phi)$ for a case when the CO mole-

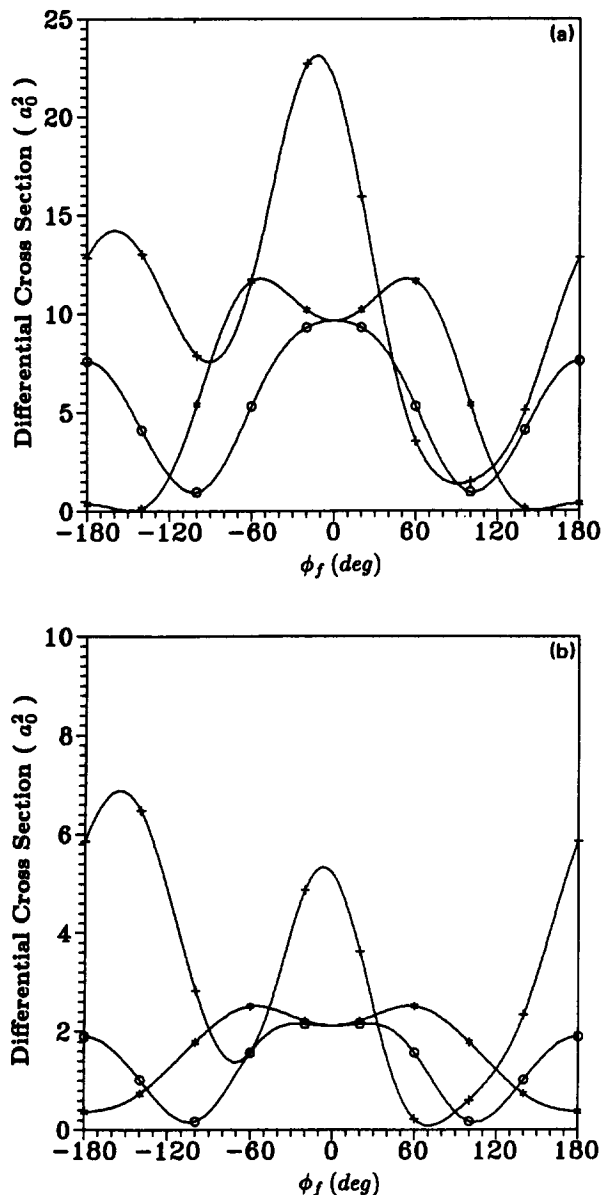


FIG. 2. The scattering cross section $\sigma(\phi)$ as a function of the azimuthal angle ϕ for a CO molecule lying flat on the surface. The curve marked with crosses is for a molecule whose axis is perpendicular to the plane of incidence. The O atom is at the left of the plane of incidence, as seen from the electron gun position. The curve corresponding to a CO molecule whose axis is in the plane of incidence is marked with circles, if the C atom points towards the electron gun, and with stars, if the O atom points towards the electron gun. (a) Scattering by surface is included. (b) Only scattering by the fixed, oriented molecule is included.

cule is tilted by 45° with respect to the normal. The curve marked by triangles shows the case when the molecule is in the plane of incidence and is tilted with the oxygen atom towards the electron gun. The differential cross section $\sigma(\phi)$ for this case is very similar to that obtained for the standing molecule.

The curve marked by squares shows $\sigma(\phi)$ for the case when the plane of the tilted molecule is perpendicular to the plane of incidence and the oxygen atom leans to the right of the plane of incidence. The dependence of σ on ϕ is now asymmetric, with a large forward peak. More electrons are scattered in a near-backward direction to the right-hand side

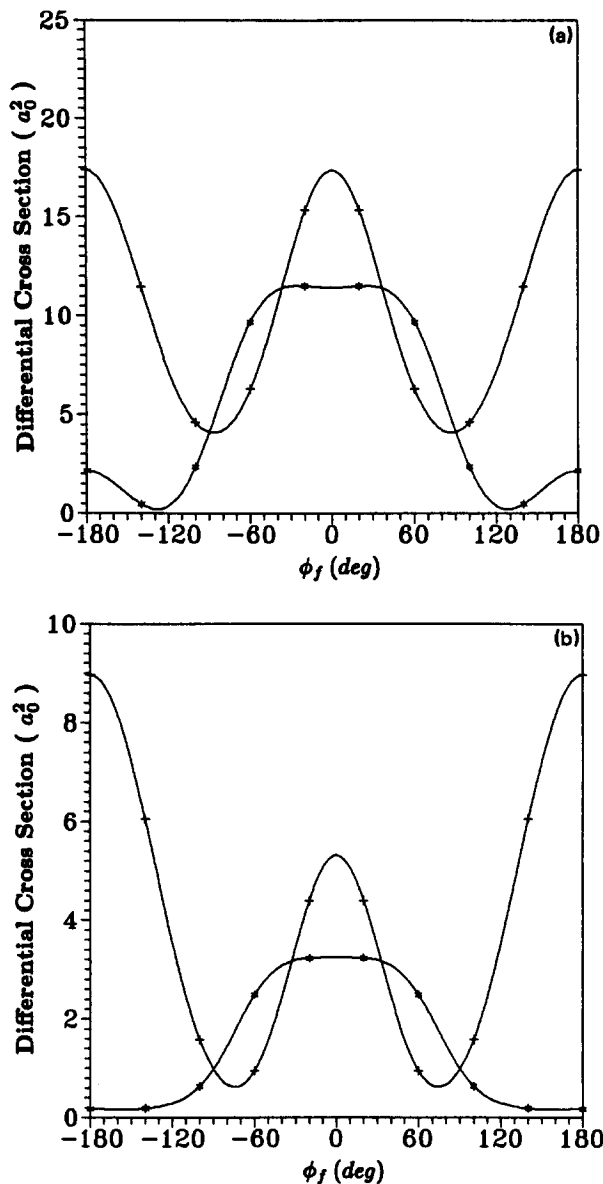


FIG. 3. The scattering cross section $\sigma(\phi)$ for N_2 lying flat on the surface. The crosses mark the results for N_2 axis perpendicular to the plane of incidence. The stars mark the case when the N_2 axis is in the plane of incidence. (a) Surface scattering included. (b) Scattering by a fixed, oriented molecule only.

of the electron gun (as seen by an observer located at the gun position) than in the case of the standing molecule.

The asymmetry in the dependence of $\sigma(\phi)$ on ϕ is sufficiently high to permit an experimentalist to determine the existence of the tilt by rotating the sample about the normal to the surface. Unfortunately the angular pattern of the scattered electrons is fairly insensitive to the magnitude of the angle of tilt.

In Fig. 4(b) we show $\sigma(\phi)$ for a fixed CO molecule in the absence of the surface. The curve for the standing molecule (marked by circles) is roughly the same as that obtained when the surface is present. The other two differ.

D. Scattering by standing and tilted N_2

Scattering by standing and tilted N_2 is very similar to that due to CO. The cross section is shown in Fig. 5.

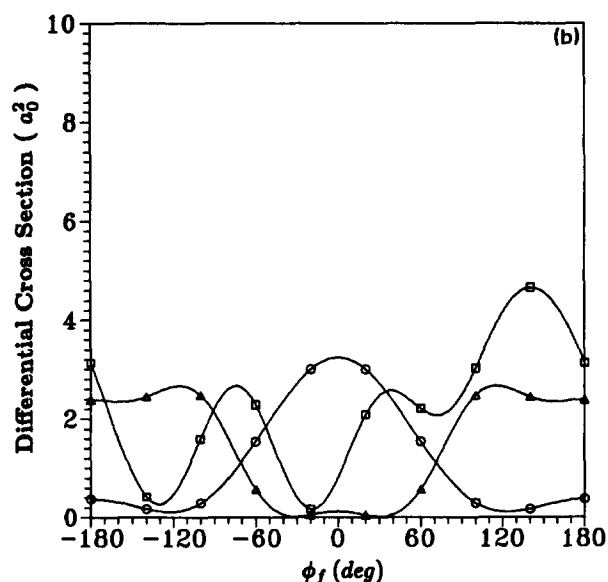
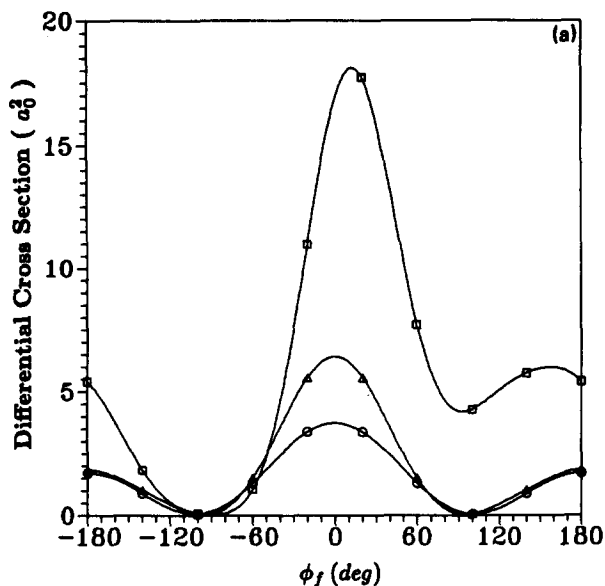


FIG. 4. Scattering cross section $\sigma(\phi)$ for CO. The circles mark the case when CO is upright with the C atom near the surface. The triangles mark the cross section for a CO tilted by 45° with respect to the normal, with the axis parallel to the plane of incidence and the O atom pointing towards the electron gun. The squares mark the cross section for a CO molecule tilted by 45° with respect to the surface, with the plane containing the molecular axis perpendicular to the plane of incidence and the O atom leaning to the right. (a) Surface scattering included. (b) Scattering by the fixed, oriented molecule only.

III. SUMMARY AND COMMENTS

The present work can stimulate two kinds of experimental inquiries: the determination of adsorbate orientation or the test of the accuracy of the present calculations. In this section we discuss the significance of the present results to such experiments.

We assume that the cross section measurements will be done in an instrument in which the sample can be rotated around an axis perpendicular to the surface and passing through its center. Thus the orientation of the surface with respect to the plane of incidence of the electron beam can be

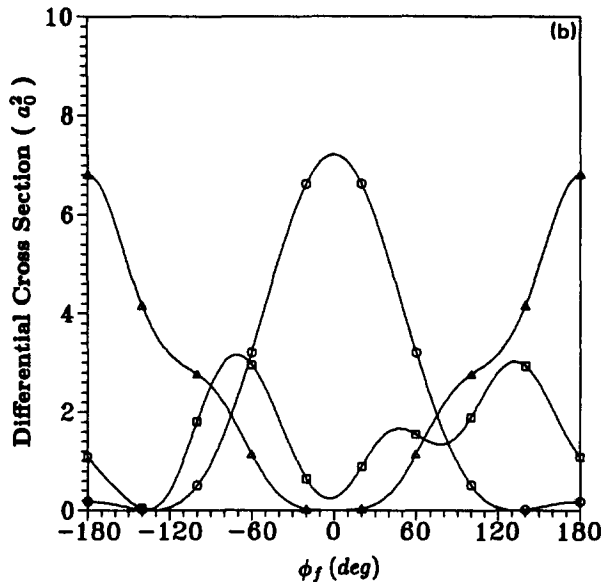
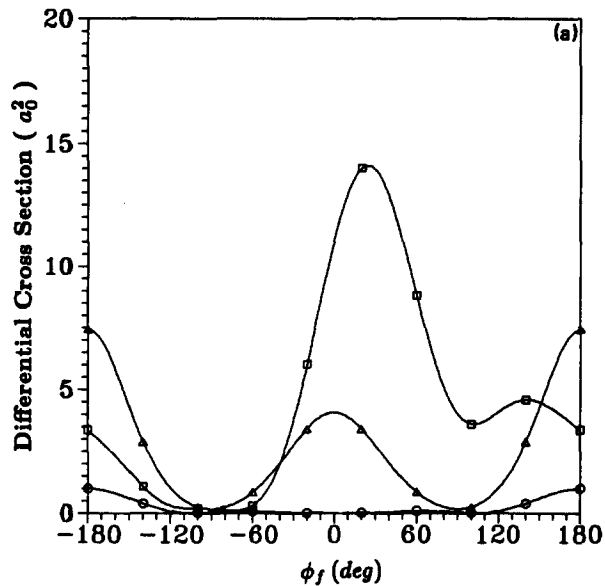


FIG. 5. Same as Fig. 4 except that N_2 replaces CO.

varied continuously. If the adsorbed molecules have a specific orientation with respect to the surface, then sample rotation also changes the orientation of the molecule with respect to the plane of incidence. We further assume that the detector can be rotated so that the azimuthal detection angle can be varied. Useful angular distribution may also be provided by using an ESDIAD instrument with a digital detection provided by using a resistive anode.⁷

The graph marked by circles in Fig. 4(a) shows that if the CO molecule is upright, the electron distribution, with respect to the azimuthal angle, is symmetric. Of course symmetry arguments alone, with no help from a quantitative theory, will predict that the angular distribution is symmetric around the forward direction as well as the fact that if the sample is rotated around an axis perpendicular to the surface, the intensity of the scattered beam will not change at any angle of detection.

It would seem, therefore, that one can determine

whether CO is upright from symmetry arguments alone. However, this assumes that a tilted CO (or N₂) molecule or one lying flat will have a *detectable* asymmetry in angular distribution. Such a statement cannot be made without a reliable calculation. Figures 2(a), 3(a), 4(a), and 5(a) show that a pronounced asymmetry exists only if the CO molecule is substantially tilted (i.e., 25° to 90°) with respect to the normal to the surface. ESDIAD work⁸ shows that CO molecules adsorbed on Ni(110) or Ru(001) may be tilted by angles smaller than 25°. The present calculations show that it will be difficult to detect such small tilt by elastic electron scattering; the asymmetry induced in the angular distribution by the molecular tilt will be too small to distinguish this situation from the case when CO is upright.

Our calculations show that if the molecule is tilted substantially the asymmetry in the angular distribution is sizable; moreover, it can be used to detect the orientation of the plane in which the molecule is tilted. To do this one must make use of the results shown in Figs. 4(a) and 5(a), which indicate that the scattering cross section is largest in the range between -40° and 180° if the plane of tilt is perpendicular to the plane of incidence. Moreover, if the oxygen is tilted towards the right-hand side of the plane of incidence (as seen from the electron gun), the electrons are mostly scattered towards the right-hand side. The angular pattern becomes symmetric if the plane of tilt coincides with the plane of incidence. Thus, by rotating the sample, hence changing the direction of the plane of tilt, we can determine when the plane of tilt is perpendicular or parallel to the surface. The same strategy can be applied when the molecule is lying flat on the surface to determine the direction of the plane of tilt and the position of the carbon and oxygen atoms in that plane. As shown in Fig. 2(a) if the plane of tilt is parallel to that of incidence and the carbon atom points towards the electron gun the cross section has a maximum in the forward direction; if the oxygen points towards the electron gun then the cross section has a minimum in the forward direction.

While the substrate often tends to orient all the adsorbed molecules in the same direction, many exceptions can exist. Thus the CO molecules may be tilted all in the same plane but the O atom may point in different directions: half of them to the left and half to the right (as seen by an observer standing perpendicular to the surface and looking perpendicular to the plane in which the molecules are tilted). If scattering by different molecules is incoherent the cross section for that system will be the sum of the curve marked by squares in Fig. 4(a) and of its reflection in a mirror located at $\phi = 0$. The total pattern will be symmetric and one might assume, erroneously, that the CO molecule is upright. However, if the

sample is rotated the intensity will change and this will not happen in the case of upright CO. Maximum intensity will be achieved when the sample is rotated so that the plane of tilt is parallel to the plane of incidence.

Another issue deserving comment is the close similarity between the angular dependence of the cross section for the adsorbed molecule (surface present) and that for an oriented molecule (surface absent). In the present model the case when the surface is present differs from the oriented one through the following processes: (a) the electron is scattered *forward* by the molecule, hits the surface, and is deflected to the detector; (b) the electron is deflected by the surface and then is scattered *forward* towards the detector; (c) the electron hits the surface, is scattered backward by the molecule, then hits the surface and reaches the detector. It turns out that the cross section for the electron to go forward, *through the molecule*, is very small, so events (a) and (b) are insignificant. Note that the forward scattering *through the molecule*, which contributes to the events (a) and (b) is not plotted in Fig. 2(b), since that would not send electrons to the detector with the gun-detector arrangement used in Fig. 1. The contribution from event (c) modifies the magnitude of the cross section, but makes only slight changes in the shape of the angular distribution. These observations explain why the presence of the surface does not cause a substantial change in the cross section. We note that this is not generally the case. Our previous calculations for the electronic excitation of H₂ and elastic scattering by H₂O show large differences between adsorbate scattering and scattering by the oriented molecule.

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