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Adsorption geometry of ethyl iodide on clean and oxygen covered Ru(001) surfaces: LEIS, XPS and TDS study

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Abstract

Ion scattering spectroscopy (LEIS) was used in conjunction with temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) for the study of the adsorption of ethyl iodide on clean and oxygen covered Ru(001) surfaces. The data suggest that ethyl iodide forms chemisorbed, physisorbed second (bilayer) and condensed multilayer on clean surface. On oxygen-precovered Ru(001) ethyl iodide molecules bond preferentially to Ru sites but very close to oxygen adatoms holding together by Coulomb forces.

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1. Introduction

The surface chemistry of halogenated hydrocarbons is receiving considerable attention for several reasons. First, these molecules serve as important precursors for preparing surface hydrocarbon intermediates [1–3] as carbon–halogen bonds (except C–F) are typically weaker than C–H and C–C bonds, consequently they can be selectively dissociated through thermal and non-thermal methods (UV irradiation) [4]. The surface chemistry of these fragments, of great importance in hydrocarbon catalysis, can then be studied in a great detail [5,6]. Second, halogenated hydrocarbons or halocarbons are well-known environmental pollutants [7] and their fundamental chemistry on solid surfaces

is relevant to environmental protection and cleanup technology. These reasons motivated us to study the adsorption mode, the dissociation process of alkyl halides at low temperature on clean and coadsorbate covered surface.

The adsorption of CH_2I_2 and $\text{C}_2\text{H}_5\text{I}$ was investigated earlier by means of thermal desorption and photoelectron spectroscopy on clean and oxygen modified Ru(001) surfaces [8–10]. The non-dissociative bonding to the surface through the iodine end of the molecules was dominant for coverage of one monolayer at the adsorption temperature of 110 K. Preadsorbed oxygen significantly increased both the desorption and the C–I bond cleavage temperature indicating that new adsorption states of halo hydrocarbon appeared on O-modified Ru(001). Oxygen atoms react with C_2H_5 to give diethyl ether and at higher oxygen coverage, acetaldehyde [10]. Similar selective oxidation products were observed in the case

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of the $C_2H_5 + O/Ag(110)$ system [11,12]. Oxygenated hydrocarbon (acetaldehyde) was also detected on Rh(111) [13,14]. In all these cases ethoxide formation plays an important role. This species decomposes via β -hydride elimination to form acetaldehyde. In the present paper the adsorption geometry and the precursor state of C–I bond breaking are discussed on clean and oxygen covered Ru(001) surfaces. Since low energy ion scattering is extremely surface sensitive (monolayer), a low energy ion scattering spectroscopy (LEIS) combined with other surface science tools, could give useful information about the surface processes [15,16].

2. Experimental

The experiments were performed in standard ultra-high vacuum system, with a background pressure of 5×10^{-10} mbar, equipped with facilities for low energy ion scattering spectroscopy, Auger electron (AES), X-ray photoelectron (XPS) and thermal desorption spectroscopies (TDS). Auger and photoelectrons were analyzed by electrostatic hemispherical analyzer (Leybold-Heraeus LHS-10). LEIS spectra were obtained using the same hemispherical energy analyzer as for XPS but with the signs of the voltage biases inverted in order to detect ions rather than electrons. The geometry of the experimental apparatus is such that the scattering angle for LEIS was 95° . The sample was placed slightly tilted with respect to the beam plane and with the incident angle set at 67° with respect to the surface normal. A Specs IQE 12/38 helium ion gun was used with the ion energy of 500 eV. The current at the sample was $0.3 \mu A$. At this conditions no significant sputtering effect was experienced. An Al $K\alpha$ X-ray anode was used for XPS. All binding energies were referred to the Fermi level with the Ru($3d_{5/2}$) peak at 280 eV. For TDS the sample was resistively heated at $5 K s^{-1}$ from 110 K to the selected temperature. The mass spectrometer was in “line of sight”.

Preparation and cleaning of the Ru(001) crystal have been described previously [8–10]. Rigorous sample cleaning was done by Ar^+ bombardment to remove irreducible oxides and common impurities. Routine cleaning from surface carbon was accomplished by cycling the crystal temperature between

900 and 1450 K in an oxygen flux which resulted in 1×10^{-8} mbar pressure rise as measured by the system's ion gauge. This was followed by annealing at 1500 K to remove adsorbed oxygen. C_2H_5I was obtained from Fluka; it was degassed by freeze-pump-thaw cycles prior to use. O_2 was obtained from Messer-Griesheim. The oxygen coverage was determined by O(1s) XP signal which is calibrated against the ideal O coverage of $p(1 \times 2)$ -O (assumed to be 0.5 ML) [17].

3. Results and discussion

3.1. Adsorption on clean Ru(001)

Previous studies showed that almost all the C_2H_5I molecules bond molecularly in submonolayer regime on Ru(001) at 110 K [10]. The integrated area of the I($3d_{5/2}$) XP signal increases linearly with the exposure. This linear correlation suggests a constant sticking coefficient regardless of the coverage (submonolayer to multilayer). Cleavage of C–I bond begins at 130 K. C_2H_5I adsorption significantly decreases the work function (~ 1.2 eV) similarly to the earlier studied halocarbon (CH_2I_2), which indicates that the molecules have positive outward dipole moment, i.e. they bond to the surface through their I-side [8].

Fig. 1A compiles representative LEIS spectra as a function of exposure for ethyl iodide adsorbed on Ru(001) at 110 K. There is a significant decrease in the intensity of the Ru LEIS signal upon adsorption of 0.2 L ethyl iodide. Similar drastic change was observed in the case of 2-iodopropane adsorbed on Ni(100) [18]. Fig. 1B displays integrated Ru LEIS signal intensity versus exposure in a large coverage region. In contrast to the XPS I($3d_{5/2}$) signal, also shown in Fig. 1B, the Ru LEIS intensity changes not linearly with exposure even at very low coverages. At around 3 L exposure the Ru LEIS signal was hardly detectable. Note that at somewhat higher incident angle (73°) the observed intensity decrease was slightly more pronounced.

Previous temperature-programmed desorption (TPD) studies on the clean surface showed the molecularly adsorbed C_2H_5I desorbs in two peaks in submonolayer regime [10]. For illustration we present some characteristic TPD features in Fig. 2. The first

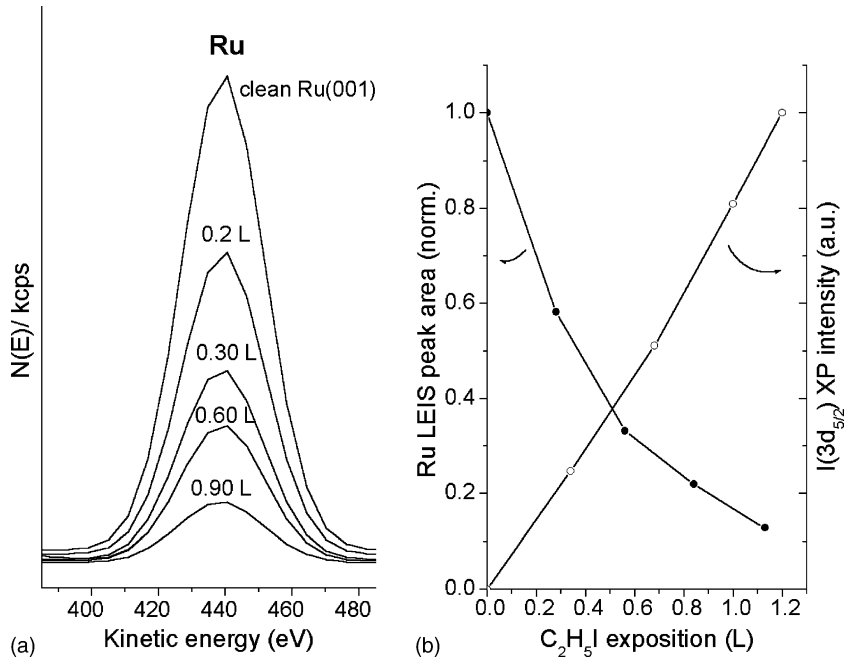


Fig. 1. LEIS spectra of Ru as a function of C_2H_5I exposure at 110 K (A). LEIS normalized intensity of Ru and XPS integrated area of $I(3d_{5/2})$ as a function of C_2H_5I exposure at 110 K (B).

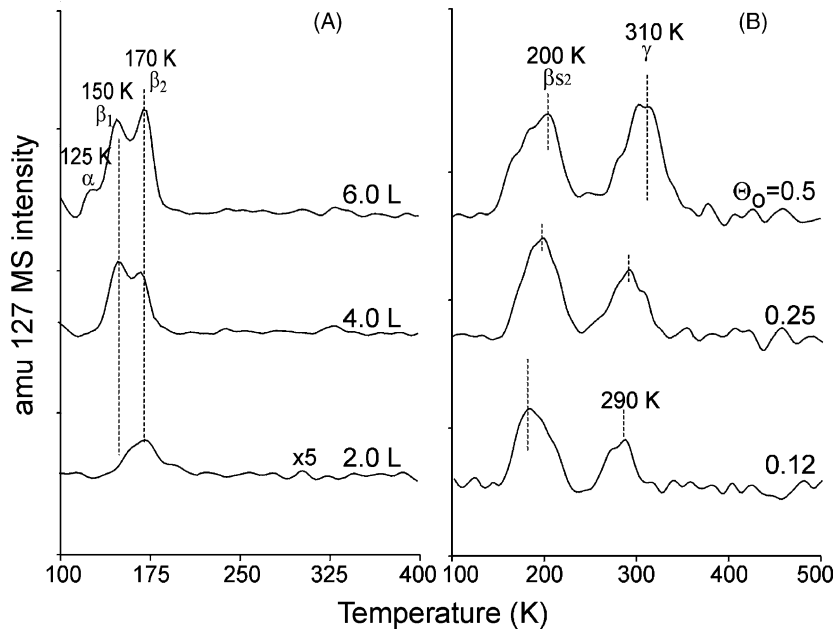


Fig. 2. TPD spectra of C_2H_5I as a function of C_2H_5I exposure on clean surface (A) and C_2H_5I desorption on oxygen covered surface. C_2H_5I exposure was 2.0 L at 110 K (B).

peak appeared at $T_p = 170$ K (β_2). With slightly increasing coverage a new desorption state developed at $T_p = 150$ K (β_1). Note that this two-peak structure was not observed in the case of CH_2I_2 and CH_3I adsorption on Ru(001) [8]. There was a new peak emerging at $T_p = 125$ K (α) on the TPD curve corresponding to 6 l dose which grows continuously with exposure. Thus, this latter peak was attributed to the multilayer.

In the light of the results we may speculate about the origin of desorption states. The former two features, β_1 and β_2 may correspond to desorptions from the chemisorbed state. The integrated peak area of β_1 is approximately equal to that of β_2 . The peak labeled β_2 appears first and its peak temperature is higher by approximately 20 K than that of β_1 . It shows that the β_2 state contains the more strongly bound molecules. Our previous studies with CH_2I_2 [7] do not suggest that there are two kinds of sites on the surface with different binding energies, thus we may assume that the difference between β_1 and β_2 originates from the intermolecular interactions in the adsorbed layer which could imply the presence of clusters or islands of $\text{C}_2\text{H}_5\text{I}$. $\text{C}_2\text{H}_5\text{I}$ has a longer side-chain than the other molecules studied before on Ru(001) (CH_2I_2 and CH_3I) revealing the character of the interatomic force. The longer chain of $\text{C}_2\text{H}_5\text{I}$ may cause the molecules bonded close to each other, and as a result, they desorb at lower temperature (β_1) as compared to molecules bonded at the perimeter of the islands or attached far from each other. The activation energy of desorption is calculated from the TDS results assuming first-order desorption process with $\nu = 10^{13} \text{ s}^{-1}$: $E_a = 36.2$ and 41.2 kJ mol^{-1} for the β_1 and β_2 peaks, respectively. The difference between the energies ($\sim 5 \text{ kJ mol}^{-1}$) may correspond to the interatomic destabilization caused by the steric effect of the side-chain. The same energy difference can be observed between the α and β_1 states, which shows that the surface excess bonding energy may be comparable with the effect of side-chains. E_a for the multilayer (29.9 kJ mol^{-1}) is in good agreement with the literature data for condensed phase (29.4 kJ mol^{-1}) certifying our assumption on the desorption kinetic parameters.

The assumption of the island formation, however, is solely based on TPD data. An alternative explanation is the formation of second layer (bilayer) structure in which the β_1 state develops on top of first chemisorbed

phase (β_2), probably with opposite orientation (ethyl down). Molecules of the second layer would also adsorb in the middle of those of the first layer, in this picture. Similar bilayer model was concluded for CH_3Br [19] and CH_3Cl [20] on Ru(001) and for $\text{C}_2\text{H}_5\text{Cl}$ [21] on Pt(111).

The highly polar molecules, such as alkyl halides, adsorbed next to each other are not expected to form islands spontaneously due to strong dipole–dipole repulsion among neighbors. The very large decrease in the intensity of Ru LEIS signal with exposure do not support the island model. According to our rough calculation the ratio of surface ruthenium atoms and adsorbed ethyl iodide molecules is approximately 20 at 1 L exposure ($\Theta = 0.05\text{--}0.06$). At the same time Fig. 1B shows that LEIS detects only 15% of surface Ru atoms after this exposure, which is much less than expected if islands were formed. In the case of an island structure, a great number of free surface Ru atoms should remain at this low coverage, on which the scattering of He ions is not influenced by $\text{C}_2\text{H}_5\text{I}_{(a)}$. We think that the decrease in Ru LEIS signal intensity is explained mostly by blocking the Ru surface atoms by adsorbate, taking into account the high incident angle used, though the alteration of neutralization probability of He due to work function changes upon adsorption may also contribute to the rapid intensity decrease of Ru signal. Note that in the presence of preadsorbed oxygen—which causes an increase in work function—Ru LEIS signal attenuates less steeply with $\text{C}_2\text{H}_5\text{I}$ exposure. The non-linearity of Ru peak area with $\text{C}_2\text{H}_5\text{I}$ coverage on clean Ru can be explained by changes in neutralization probability due to an electronic effect in the presence of the adsorbate. An alteration in the orientation of adsorbed ethyl iodide with coverage could slightly influence the decrease and deviation from linearity of LEIS signal intensity. Orientation change was established by RAIRS experiments for the adsorbed $\text{C}_2\text{H}_5\text{I}$ on Pt(111) at 100 K as the surface coverage was increased [22]. This phenomenon is probably valid for the Ru(001) surface, too.

3.2. Ethyl iodide adsorption mode in the presence of coadsorbed O

The surface structure of adsorbed oxygen has been extensively investigated in the past. Oxygen adsorbed

on Ru(001) surface gives two different LEED structures depending on the surface coverage. At 0.25 ML coverage a sharp $p(2 \times 2)$ LEED image emerges, at 0.5 ml the surface is characterized by $p(1 \times 2)$ structure. Below the onset of the perfect $p(2 \times 2)$ mesh the surface is covered by O-islands with diffuse $p(2 \times 2)$ image [17,23,24]. In present work we present some LEIS data on the O/Ru(001) system. Fig. 3 shows the changes in LEIS spectra as a function of oxygen exposure at 300 K, which leads to coverage from approximately 0.05–0.50 ML. LEIS peaks for O and Ru are both observed, approximately at 275 and 450 eV. The Ru signal decreases rapidly as the oxygen exposure is increased up to 3–4 L. This variation of the Ru signal as a function of oxygen exposure is illustrated more clearly in Fig. 4, which displays the LEIS peak areas for both ruthenium and oxygen, normalized to the clean surface and to that saturated with O, respectively. This figure also shows that the absolute LEIS signals for Ru correlate in a linear fashion with those of O over most of the oxygen coverage range. The same trend was observed on Ni(100) surface [18], where it was concluded that the neutralization probabilities for the scattered He ions are unaffected by several factors (work function, geometric changes).

Next, the adsorption process of ethyl iodide was investigated by LEIS method on oxygen covered

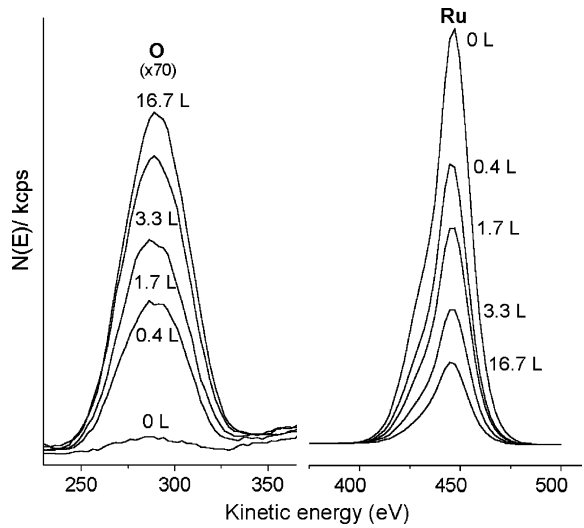


Fig. 3. LEIS spectra of O and Ru as a function of oxygen coverage at 300 K.

Ru(001) surface. The intensity of both ruthenium and oxygen LEIS signals decreased with ethyl iodide exposures. Detailed experiments were performed at fixed oxygen coverage where the oxygen structure exhibits $p(2 \times 2)$ structure ($\theta = 0.25$). Fig. 5 shows the ethyl iodide coverage-dependent LEIS data obtained at this oxygen concentration. One of the

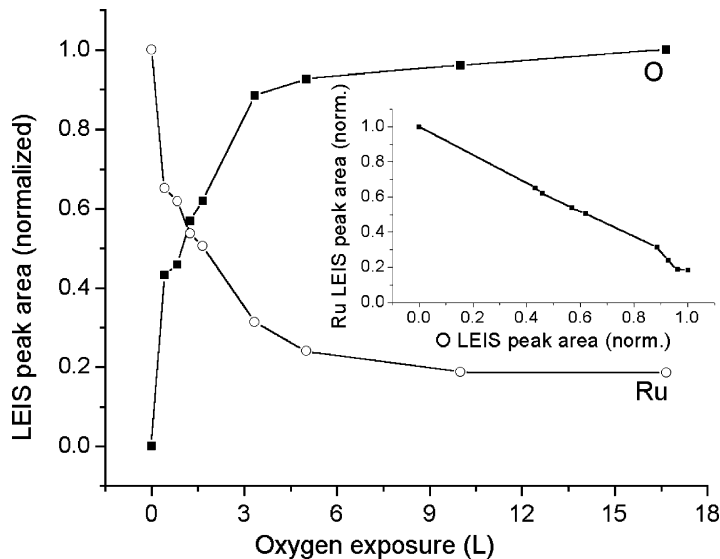


Fig. 4. The change of LEIS peak areas of O and Ru after different oxygen exposures at 300 K. The inset shows how the normalized Ru intensity varies as a function of normalized O LEIS intensity.

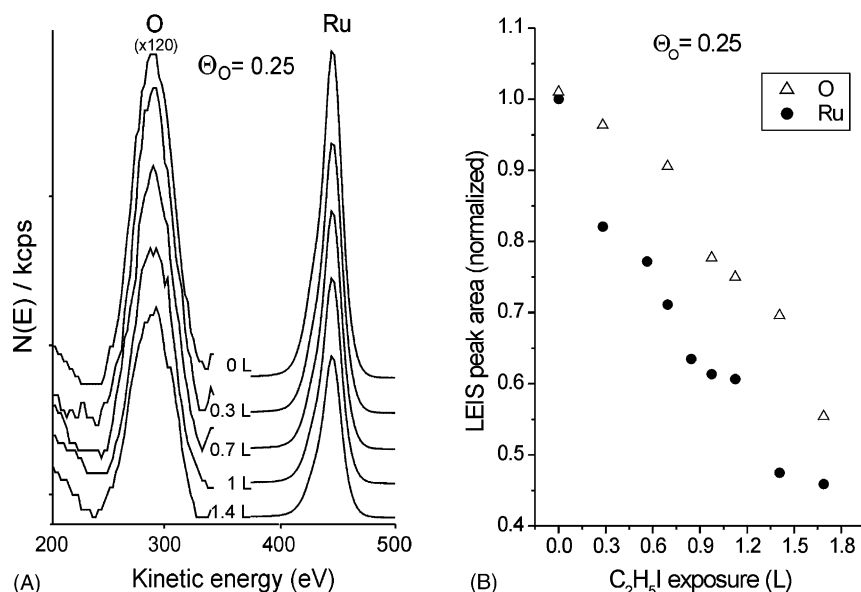


Fig. 5. LEIS spectra of O and Ru as a function of $\text{C}_2\text{H}_5\text{I}$ exposure on O/Ru(001) system ($\Theta_{\text{O}} = 0.25$) at 110 K (A). Normalized Ru and O LEIS intensities as a function of $\text{C}_2\text{H}_5\text{I}$ coverage on oxygen covered Ru(001) at 110 K (B).

most interesting features is that the Ru and O signals change almost linearly in the whole exposure range. The intensity decrease for the Ru signal was much more pronounced than for that of O (Fig. 5B). This picture suggests that the ethyl iodide molecule bonds preferentially to metal sites which was also experienced for the adsorption of 2-iodopropane on Ni(100) [18,25]. In our O/Ru(001) system small but linear intensity change was detected for oxygen, too, even at low exposures (Fig. 5B). This behavior is in contrast with the case of Ni(100) surface, where the Ni signal decreases significantly while the O signal remains almost constant at least at low 2-iodopropane exposures [25]. We are inclined to think that in the case of O/Ru system ethyl iodide bonds to Ru but close to oxygen atoms, therefore shields them (Fig. 6).

Former TPD spectra obtained on oxygen covered Ru(001) surface support this assumption. The desorption characteristics of the $\text{C}_2\text{H}_5\text{I}$ markedly changed in the presence of adsorbed O at any occupancy of the surface [10]. Some TPD results are displayed on Fig. 2B. New desorption features appeared indicating the presence of strongly stabilized forms.

Below $\Theta_{\text{O}} = 0.12$ ML the β_2 peak shifts to higher temperature, but by the further increase of the O

coverage a new feature also appears at around 300 K (γ). This latter state is attributed to $\text{C}_2\text{H}_5\text{I}$ molecules bonded inside the oxygen islands. Similar conclusion could be drawn for the adsorption of CH_2I_2 on O-covered Ru(001) surface [10]. The average distance between the neighboring O-rows is 4.6 Å which is perfect for the formation of extended 2D structures containing O and the corresponding

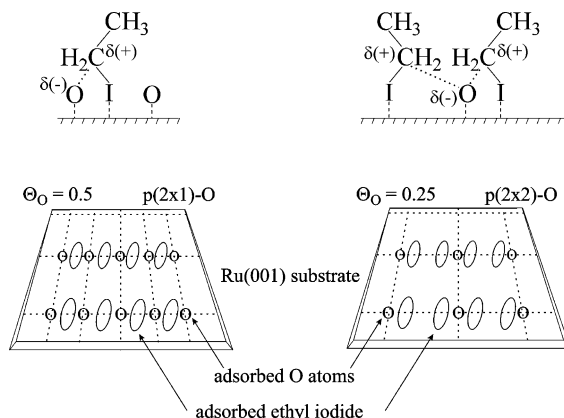


Fig. 6. Schematic diagram for adsorption of $\text{C}_2\text{H}_5\text{I}$ on oxygen covered Ru(001) surface.

hydrocarbon species. Adsorbed O is known to increase the work function of Ru(001) surface indicating partial negative charge located on O [17]. The driving force of the formation of this structure is assumed to be the Coulomb interaction between the oppositely charged O- and C-center of the adsorbed molecules. A similar interaction is thought to be responsible for the emergence of β_{s2} peak in Fig. 2B. This is the dominant peak characteristic for the C_2H_5I desorption up to $\theta_O = 0.25$ ML, the saturation of the $p(2 \times 2)$ structure. The desorption temperature of C_2H_5I molecules adsorbed in that form is slightly higher than that on clean Ru(001) suggesting only a weak perturbation of the bonding of the molecule to the surface by somewhat more distant oxygen atoms. The proposed scheme is displayed on Fig. 6, which is supported by our LEIS experiments.

The Coulomb interaction discussed above modifies not only the desorption characteristics of C_2H_5I on O-covered surface, but also the C–I bond dissociation mechanism. It was observed that the decomposition temperature of C_2H_5I was higher on Ru(001) saturated with oxygen. The XPS peak characteristic for atomic iodine appeared above 250 K which is higher by 100 K than the corresponding value on clean surface [10]. We suppose that the rupture of the C–I bond occurs in S_N2 reaction of O and ethyl iodide which are held together by Coulomb forces, as represented in Fig. 6. This proposed intermediate may lead to the formation of surface alkoxy species which reacts further to final oxygenated products, such as diethyl ether and acetaldehyde.

4. Conclusion

Ion scattering spectroscopy results with harmony of thermal desorption and X-ray photoelectron spectroscopy suggest that ethyl iodide forms chemisorbed, second physisorbed (bilayer) states and multilayer on clean surface. The preadsorbed oxygen stabilized and induced new adsorption state of ethyl iodide. LEIS studies indicated that ethyl iodide bond preferentially to metal sites close to oxygen adatoms holding together by Coulomb forces which is responsible for stabilization effect. The decrease in Ru LEIS signal intensity is explained by blocking of the Ru surface by adsorbates.

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