

DISSOCIATIVE ELECTRON ATTACHMENT IN ALCOHOLS AND ETHERS: ITS RELATIONSHIP TO RYDBERG STATES

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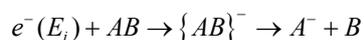
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Abstract. *A dramatic difference was observed in the reactivity of alcohols and ethers toward free electrons. Whereas the lowest core-excited state of the negative ion - a $^2(n,3s^2)$ Feshbach resonance - of the alcohols readily dissociates by losing a hydrogen atom, ethers show no observable signal from this resonance. This difference in reactivity has a parallel in the anomalous shapes and energies of the parent states of the Feshbach resonances, the $^1(n,3s)$ Rydberg states of the neutral alcohols and ethers. We explained this anomaly by means of potential surfaces of the alcohols and ethers calculated using the TD-DFT method as a function of the dissociation coordinate. The lowest excited state of alcohols was found to be repulsive, as a consequence of an avoided crossing between the $3s$ and $3p_x$ Rydberg configurations, whereas a barrier to dissociation was found in the ethers. Rydberg-valence mixing and avoided crossings are decisive in determining the shapes of the potential surfaces. It is concluded that the reactivities of alcohols and ethers toward free electrons are rationalized by assuming that the potential surfaces of the daughter Feshbach resonances closely follow those of the parent Rydberg states, i.e., the lowest Feshbach resonance is repulsive, but a barrier occurs in ethers. The potential surfaces of both the Rydberg states and the Feshbach resonances thus differ dramatically from the non-dissociative surface of the grandparent $^2(n^{-1})$ positive ions, despite the nominally non-bonding character of the Rydberg electrons.*

INTRODUCTION

The process of dissociative electron attachment (DEA) to a general molecule, AB , can be represented by the scheme



where E_i is the energy of the incident electron and AB^- is an intermediate short-lived anion also called a resonance. The interest in this process has increased due to emerging applications in technology [1] and the need to understand radiation-induced damage to living tissue [2].

The current paper studies the DEA mediated by Feshbach resonances in the 5-15-eV energy region. In this case the incoming electron generates an electronic excitation in the target molecule and itself becomes trapped by this excitation. The DEA bands found in this region are hard to assign because of the lack of the corresponding features in other channels of electron scattering. The situation is further complicated by the fact that at these energies dissociation into various fragments is thermodynamically possible, and often several fragments are detected arising from the same resonance. In the present case this is not possible and we shall rely on the relation of daughter and grandparent states for the assignment. In small molecules it has been possible to assign the bands without any doubts, because the DEA bands have sharp vibrational structure which is similar to that of a Rydberg excited state of the neutral molecule (the parent state) and that of the photoelectron band of the positive ion (the grandparent state). Despite the somewhat exotic nature of the Feshbach resonances they are the main pathway of dissociation, especially for saturated compounds [3,4].

There is a considerable body of scientific data on DEA of polyatomic molecules [5,6], with many of the observed bands being attributed to the Feshbach resonances. Still very little information about the detailed mechanism of dissociation is available, with water being one notable exception [7].

The present paper deals with the dissociation mechanism of the Feshbach resonances in the case of alcohols and ethers. First we make the striking experimental observation that the lowest Feshbach resonance $^2(n,3s^2)$ yields strong (M-1) signal in the alcohols, but no DEA signal in the ethers. We then note that this experimental observation has an analogy with the spectroscopic properties of the parent states of Feshbach resonances - the Rydberg states. We also calculate the potential energy curves and two dimensional potential surfaces for the Rydberg states in function of the O-H and O-C bond distances and show that they explain the experimental observation as long as one assumes that the Feshbach resonance surfaces have the same shape as the Rydberg states [8].

METHODS EXPERIMENTAL

The dissociative electron attachment spectrometer used to measure the yield of mass-selected stable anions as a function of electron energy has been described previously [4, 10, 11]. It employs a magnetically collimated trochoidal electron monochromator [12] to prepare a beam of quasi-monoenergetic electrons, which is directed into a target chamber filled with a quasi-static sample gas. Fragment anions are extracted at 90° by a three-cylinder lens and directed into a quadrupole mass spectrometer. The energy scale was calibrated on the onset of the O/CO₂ signal at 4.0 eV. The electron current was around 100 nA and the resolution about 150 meV. Photoelectron spectra were recorded with a modified Perkin Elmer PS18 HeI photoelectron spectrometer. Electron energy loss spectrum (EELS) was recorded with a spectrometer using hemispherical electron-energy selectors [13].

Calculations

The calculation were performed using the Gaussian03 package [14]. The excited state calculations were performed using the time-dependent density functional theory (TD-DFT) PBE0/6-311++G(3df,3p) model, the geometry optimizations using the DFT

B3LYP/6-311+G(2df,2p) model, as implemented in the Gaussian 03 package [14]. This model has been tested and found to satisfactorily reproduce both valence and low-lying Rydberg states of a number of molecules [15]. This conclusion was confirmed in this study. Our calculated transition energies for the $3s$ and $3p_x$ states of methanol lie 0.12 and 0.36 eV below our experimental values from the electron energy loss spectrum and a similar agreement is obtained for dimethyl and diethyl ethers when compared to the absorption spectra [16].

Potential curves were obtained by calculating the transition energies cover a range of O-H and O-C distances and adding them to the ground state energy calculated with the same model. Only the O-H and O-C distances were varied, the remaining geometrical parameters were not re-optimized (a rigid scan).

The energy of the positive ion was calculated using the same model and used to plot the potential curve of the ground electronic state of the cation. To calculate the two dimensional potential surfaces, the 6-311+G(2df,2p) basis-set was employed. This reduces significantly the necessary CPU time without significant change to the shape of the potential surfaces.

RESULTS AND DISCUSSION

The energy relation between the grandparent ion energies and those of the Feshbach resonances is detailed in ref. [8]. The usefulness of this relation is illustrated in Fig. 1. For illustration the case of ethanol and two amines (diethylamine and *tert*-butyl-amine) is presented. It can be observed that the bands in the DEA spectra follow closely the trend of the 1st photoelectron band. Using the reasoning shown in ref. [8] these bands are assigned to $^2(n,3s^2)$ Feshbach resonances. This observation is not restricted to the substances presented in Fig. 1, but they extend to the entire class of alcohols and amines that we have studied so far [3, 4]. The relation allows the assignment of the next two DEA bands in the case of methanol and of the band at 7.8 eV in the case of ethanol. But these bands do not make the object of this article and their behavior is discussed in more detail elsewhere [3, 4].

In the case of diethylether no DEA bands are observed at the predicted energy of the 1st photoelectron band. The continuous and the dashed arrows above the Et-O-Et DEA spectrum in Fig. 1 indicate the expected positions of these resonances. We conclude that in the case of diethylether the Feshbach resonances associated with the 1st and 2nd photoelectron bands do not lead to observable dissociation. The band observed at 9 eV corresponds to a Feshbach resonance with a hole either in a σ_{C-C} orbital or σ_{C-H} orbital. The associated photoelectron band lies in a region commonly named ' σ -mountain' since it consists of several broad overlapping bands corresponding to ionizations from sigma orbitals localized on the C-C and C-H bonds. Consequently no clear-cut assignment of the individual photoelectron bands can be made and the grandparent state for the Feshbach resonance cannot be determined. The difficulty in the assignment is increased by the presence of high-lying shape resonances in this energy region. Since these resonances generally have an autodetachment rate too fast to permit dissociation, we favor the assignment to Feshbach resonances. This observation is not restricted to the present ether but it applies to all ethers studied in our laboratory so far, up to dibutylether [9].

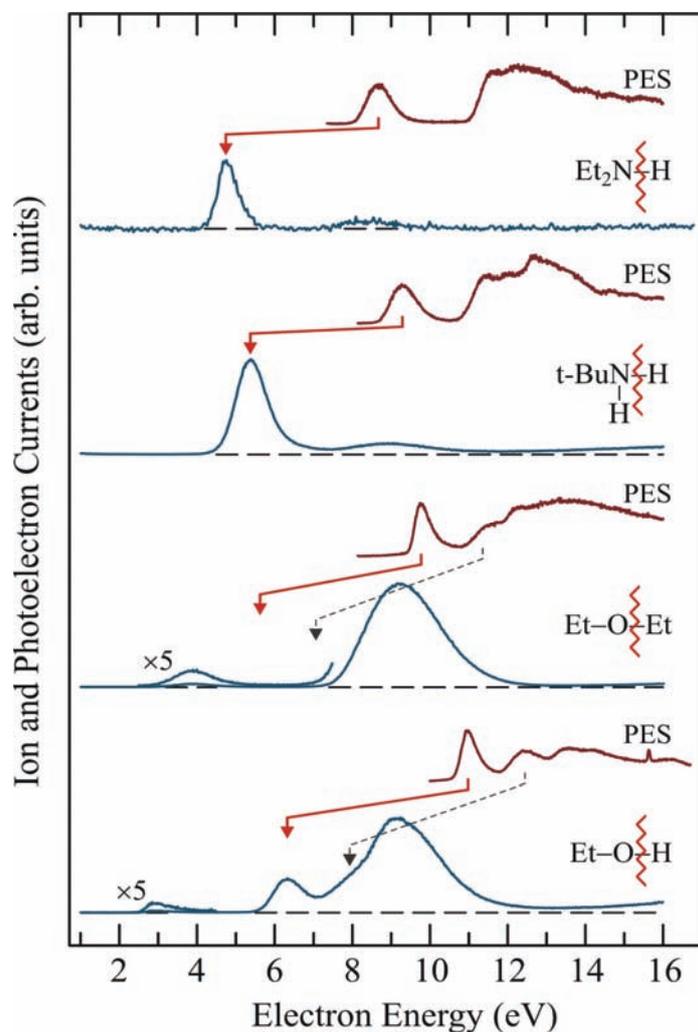


Fig. 1. Photoelectron spectra (PES) and DEA spectra of the compounds indicated. The bonds being broken are indicated in the formulas, the charge remains on the O or N containing fragment. Arrows indicate the relation between the grand-parent $^2(n^{-1})$ positive ion states and the daughter $^2(n,3s^2)$ Feshbach resonances. (The weak bands at 3 eV in ethanol and 4 eV in diethyl ether are due to shape resonances [4, 9].) The figure is taken from Ref. [8].

A helpful indication towards understanding these observations is gained by observing that a related observation has been made for the parent Rydberg states [16]. Analyzing the term values and VUV spectra, Robin has noticed that in water and alcohols the lowest $^1(n_o, 3s)$ Rydberg states are unusually low in energy, broad and featureless, as compared with the photoelectron spectrum. In contrast, for ethers the lowest Rydberg bands

behaved normally. His conclusion was that these Rydberg states are influenced by the conjugate $^1(n_O, \sigma^*)$ valence promotions in the alcohols and water while in the ethers this perturbations are not observable. To illustrate this observation we present a comparison between the photoelectron spectrum and the energy-loss spectrum for methanol in Fig.2. There is a marked difference between the 1st photoelectron and the associated band in the energy-loss spectrum. While the 1st energy loss band is broad and structureless, the next two bands have the sharp vibrational structure similar to the 1st photoelectron band. This leads to the conclusion that the observed $^1(n_O, 3s)$ Rydberg state is affected by mixing with a σ^* valence state.

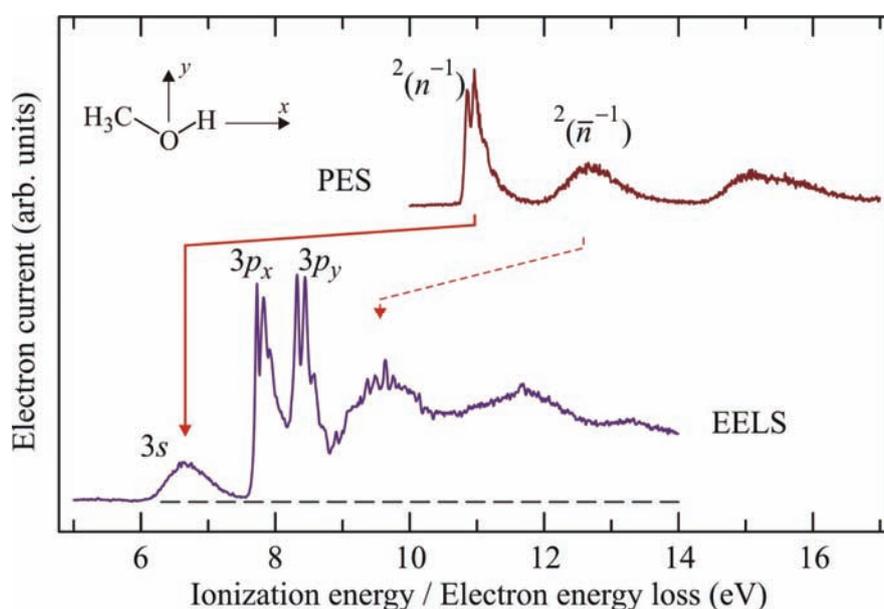


Fig. 2. The photoelectron (top) and the electron energy loss spectrum of methanol (the latter recorded at a scattering angle of 0° and a residual energy of 10 eV).

To gain further insight into the reason for the different behavior of the Rydberg states, we have calculated the potential energy surfaces for some ethers. To simplify the calculations, we have chosen as model compounds methanol and ethylmethylether instead of the ethanol and diethylether presented in Fig. 1. This change does not affect our argument since we found that the observations apply to all alcohols and ethers. These potential energy surfaces are presented in Figs. 3 and 4.

Figure 3 shows the calculated potential energy curves for methanol in function of the O-H bond distance. The lowest one is for the ground state of the neutral molecule, followed by the first two excited states. The top most one belongs to the $^2(n-1)$ cationic state. The dashed line present the visually estimated diabatic curves. Our calculations explain entirely the energy-loss spectrum in Fig.2. They show that the 3s band is structureless while the $3p_x$ and $3p_y$ bands can support vibrational structure. The calculated

$3p_z$ state has a energy only slightly higher than $3p_y$, and a very low oscillator strength explaining the fact that is not well observed in the energy-loss spectrum. To improve the clarity of the figures, the potential energy curves of the $3p_y$ and $3p_z$ states are not presented in Fig. 3 but they have a shape similar to that of the positive ion.

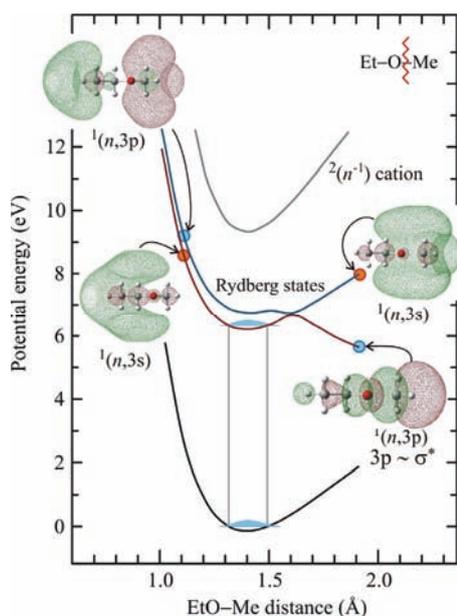


Fig. 3. Potential energy surface of methanol (bottom curve), its two lowest excited states, and the ground state of the cation (top curve), shown as a function of the O-H distance. The zero of energy has been chosen at the lowest vibrational state of neutral molecule.

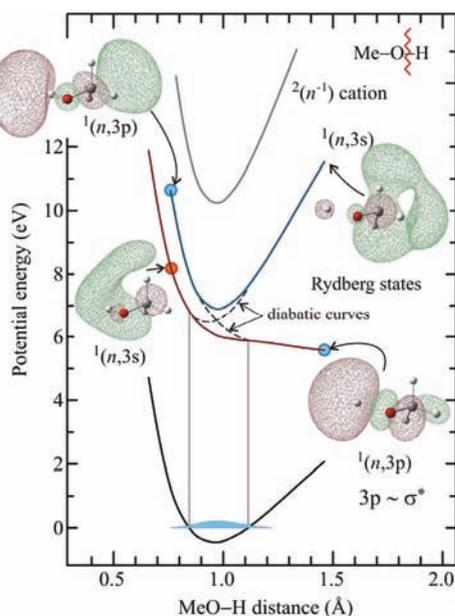


Fig. 4. Same as Fig.3. but for methyl ethyl ether.

There is a marked difference between the curves of the alcohol in Fig. 3 and that of the ether in Fig. 4. In the case of the ether a dissociation barrier can be observed on the $1(\bar{n}, 3s)$ curve, explaining why the VUV band associated with this state has vibrational structure in ethers.

The molecular orbital diagrams are useful in determining the nature of the excited state and in Figs. 3 and 4 they are shown for two O-H and O-C bond distances, one shorter and one longer than the equilibrium bond length. For both compounds the orbitals for the 1st excited state are 3s-like. They do not enclose completely the core (the degree of enclosure depending on the iso-value chosen for representation) because of the non-

spherical core. The orbitals of the second excited state are clearly $3p_x$ -like. The ordering is in agreement with the spectroscopic data presented in Fig. 2. In the case of larger bond distances that the equilibrium geometry the ordering is reversed, with the lower one resembling a $3p_x$ orbital and the higher one a $3s$ one. This is a clear sign for the presence of an avoided crossing between the involved states, since both have A'' symmetry.

As a sideline we note that in the case of the ether the details of the potential curve for the 2nd excited state are more complex than those of methanol. There is a marked difference between the diagram associated with this state and the corresponding one in alcohol. While at lower O-C bond distances it resembles more a $3p_x$ orbital, at higher bond distances it is more similar to a σ orbital. Additionally we notice the presence of a shallow double minimum in the curve. All these observations lead to the conclusion that another avoided crossing with a strongly repulsive σ^* state is present. The presence of the repulsive σ^* state also perturbs higher-lying A'' Rydberg states (not shown in Fig.4) manifested by the irregular shapes of the potential energy curves. But all these details of the potential energy curve do not affect our main conclusion, namely that the 1st excited state is dissociative in methanol while it is bound in ether.

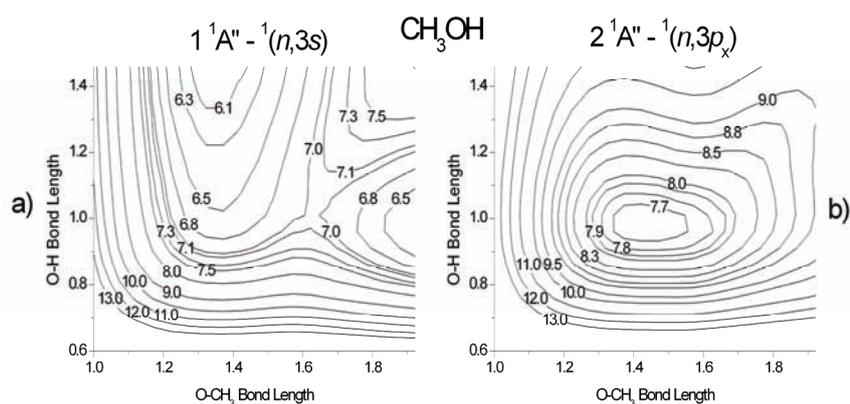


Fig. 5. Contour plots of selected excited states for methanol. The contour values are in eV. a) $1^1A'' - 1(n, 3s)$ excited state; b) $1^1(n, 3p_x)$ excited states.

The present curves, particularly for the ether (Fig.4) are also remarkably similar to those of the $^3\Pi_u$ manifold of O_2 [17]. The shapes of the O_2 curves were explained as a consequence of pre-dissociation of the nominally bound Rydberg curves by a strongly repulsive valence curve, that is, a consequence of avoided crossings resulting from Rydberg-valence coupling. This suggests that also in the present case the repulsive nature of the nominally $3s$ states, the barrier to dissociation in the ether, and the double minimum on the upper state in the ether, can all be understood as a result of avoided crossings.

To explain the main experimental observation of this paper, namely that the fact that the $^2(n, 3s^2)$ Feshbach resonance gives rise to strong DEA signal in the alcohols, but no detectable DEA signal in the ethers, we need to assume that the main features of the Rydberg states presented in Figs. 3 and 4 also applies to the Feshbach resonances. This

assumption is not unreasonable since adding an extra electron to a diffuse orbital is not expected to contribute to bonding and consequently does not influence the shape of the potential energy curves.

We have also calculated the potential curves for the higher-lying Rydberg states, the $A' {}^1(\bar{n}, 3s)$ and ${}^1(\bar{n}, 3p_x)$ where \bar{n} is the $2p_y$ -like a' lone pair orbital on the O atom. The results were similar in terms of the shapes to the curves discussed above, the nominally bound $3s$ state being dissociative in the alcohol and not dissociative in ether. These results are in line with the observation of a DEA band assigned as ${}^2(\bar{n}, 3s^2)$ in alcohols and its absence in ethers (see Fig. 1).

A deeper understanding is provided by the potential surfaces in function of both O-H and O-C bond lengths. Fig. 5 shows the contour plots for two dimensional potential energy surfaces of several excited states for methanol. The plotted surfaces are ${}^1(n,3s)$, ${}^1(n,3p_x)$, surfaces where multiple minimas have been detected, indicative of avoided crossings.

Following the stretching along the O-C coordinate a barrier to dissociation on the potential energy surface of the ${}^1(n,3s)$ excited state is encountered. The ${}^1(n,3p_x)$ has a similar shape to that of the positive ion. The shape of the surfaces along the O-C stretch in methanol is similar to that of the O-C bond in ethers. But there are some differences between the two cases. While in ethers the $3p_x$ state presented a shallow double minimum, indicative for the presence of two avoided crossings, in methanol the double minimum seems to be reduced up to the point of becoming a plateau. There is no reason why this second avoided crossing should be missing from methanol since the two bonds are so similar. We conclude that in methanol the repulsive σ^* state is present but the coupling term between the σ^* and $3p_x$ states is higher.

The presence of a barrier along the O-C coordinate explains one more experimental observation. Dissociation in methanol can also proceed through the O-C bond breaking, with the generation of the OH⁻ anion. The formation of the OH⁻ anion proceeds only from the 3rd Feshbach resonance located at around 10.7 eV [3, 4 18]. If we assume that the features of the Feshbach resonances are similar to our calculated potential energy curves for Rydberg states, the same assumption that has been made for O-C bond breaking in ethers, then it is expected that OH⁻ anion should appear only at the 10.7 eV resonance and not at the lower ones, since there is a barrier in the breaking of the O-C bond.

The ${}^1(n,3s)$ potential energy surface shown in Fig. 5 has an interesting property. The least energy path along the one of the coordinates seems to be independent with respect to the other coordinate. That means that the breaking of the O-H and O-C bonds can be treated independently. Since there are no calculations concerning the potential surfaces of the Feshbach resonances for methanol, this observation allows us to compare our results with those obtained for water, where the potential surfaces for the Feshbach resonances [7] and Rydberg states [19] are available. A comparison between the lowest A'' Rydberg states of water and methanol reveals that they are both dissociative when the O-H bond is stretched. Also, for H₂O, the potential surface for the 1st (2B_1) Feshbach resonance (see fig. 22 top right corner, in ref. [7]) and that for the parent Rydberg state (see fig. 5 in ref. [19]) have a similar shape. Consequently it is not unreasonable to expect that the potential surface for the 1st Feshbach resonance of methanol will be similar to that of the parent Rydberg state, supporting the assumption that has been made in this article.

Figs. 6 and 7 show the potential surfaces for the first four singlet excited states of A'' and A' symmetry respectively of methylethylether. For A'' symmetry the surfaces have been identified as ${}^1(n, 3s)$, ${}^1(n, 3p_x)$, ${}^1(n, 3p_y)$ and ${}^1(n, 3d)$ respectively. The 1st A' state has been identified as ${}^1(n, 3p_z)$ at bond lengths close to the equilibrium values and ${}^1(\bar{n}, 3s)$ at longer bond lengths. Since these two states have both A' symmetry a transition point is expected to appear on surface of the 1 A' state. But no such point has been detected in our calculations. The 2nd A' state has been identified as ${}^1(\bar{n}, 3p_x)$. The other two states show a strong configuration interaction mixing between transitions arising from the n and \bar{n} molecular orbitals (the two lone pairs of the oxygen) making their assignment very difficult.

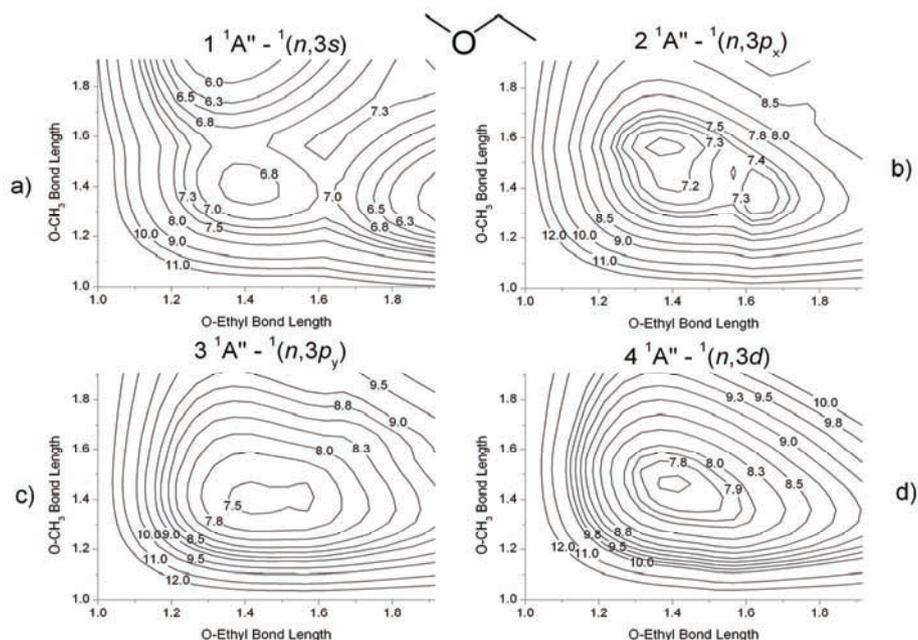


Fig. 6. Contour plots of the first four A'' excited states for methylethylether. The contour values are in eV.

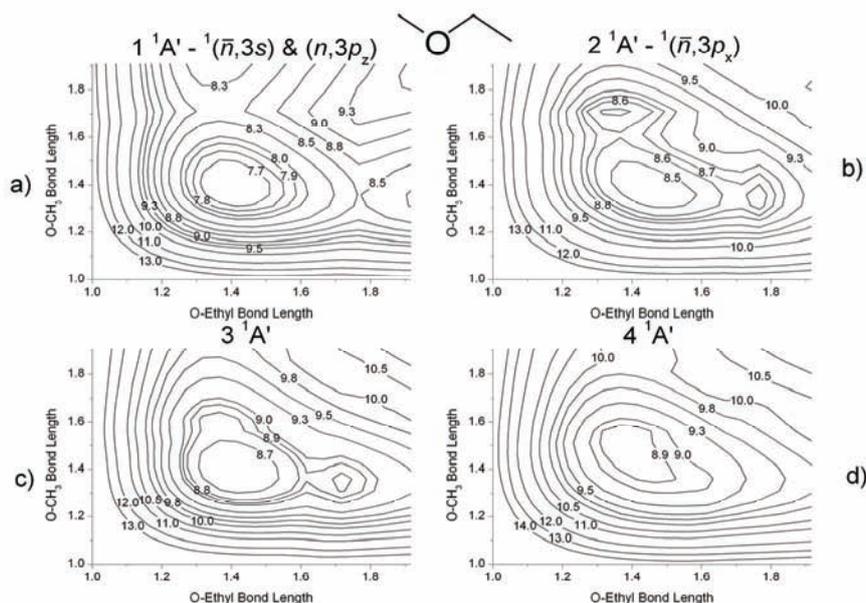


Fig. 7. Contour plots of the first four A' excited states for methylethylether. The contour values are in eV.

For the $2^1 A''^1(n, 3p_x)$ and $3^1 A''^1(n, 3p_y)$ surfaces a double minimum can be observed for stretching of both O-C bonds being more pronounced for the O-Ethyl bond. Similarly to the case shown in fig. 4 we interpret the presence of these double minima as an indication for the presence of an avoided crossing with a strongly repulsive σ^* state. The 4th state of A'' symmetry has a only one minimum and the shape is similar to that of the cationic core suggesting that, in contrast to the $2^1 A''$ and $3^1 A''$ states, is unaffected by the presence of a repulsive σ^* state. The study of the 2nd – 4th A' states shown in fig. 7 also reveal the presence of double minima along the elongation of both O-C bonds. They are more visible than for the A'' states.

CONCLUSIONS

We calculated the potential energy surface for methanol and ethylmethylether in an attempt to explain the observed differences in DEA. While these calculations do not refer directly to the Feshbach resonances that appear in DEA spectra, they can be used indirectly to explain the different behavior. While in the case of O-H bond breaking in alcohols no barrier is observed for $^1(n, 3s)$ and $^1(\bar{n}, 3s)$ Rydberg states, in the case of O-C bond breaking in ethers a significant barrier seems to be present.

The difference in reactivity towards free electrons between alcohols and ethers leads to the conclusion that in the case of methanol the lowest Feshbach resonances (with holes

in the lone pair orbitals of the oxygen) are pre-dissociated by a repulsive resonant state with a σ^* occupation, while in the case of ethers the repulsive surface comes at longer bond lengths generating an activation barrier. A related conclusion has been made for the parent states of the Feshbach resonances, the Rydberg states of the neutral molecules, where data from VUV spectra lead to the deduction of strong Rydberg - σ^* valence mixing for water and alcohols, but not for ethers [16].

For methanol the potential curves for $^1(n, 3s)$ and $^1(\bar{n}, 3s)$ Rydberg states along the O-C dissociation coordinate show the presence of a barrier. This barrier leads to the observed differences between dissociation into the $\text{CH}_3\text{O}^\cdot$ fragment and dissociation into the OH^\cdot fragment.

A comparison between the potential surfaces of $^1(n, 3s)$ Rydberg state for water and methanol reveals the fact that they are dissociative when the O-H bond is stretched. Also, the similarity between the potential surfaces of the 1st Feshbach resonance and its parent Rydberg state for water suggests that it is very likely that, for methanol, they will behave in the same manner. As an outlook, it would be interesting to calculate directly, for methanol, these potential curves of the Feshbach resonances using a scattering calculation such as the R-matrix theory yielding both their energy and the auto-detachment width.

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DISOCIJATIVNI ZAHVAT ELEKTRONA KOD ALKOHOLA I ETERA: POVEZANOST SA RIDBERGOVIM STANJIMA

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Uočena je dramatična razlika kod reaktivnosti alkohola i etera u odnosu na slobodne elektrone. Kod alkohola, najniže stanje negativnog jona sa pobuđenim atomskim ostatkom - $a^2(n,3s^2)$ Feshbach rezonanca – lako disosuje gubljenjem vodonikovog atoma, dok kod etera nije opažen signal koji potiče od ove rezonance. Ova razlika u reaktivnosti može se povezati sa anomalnim oblikom i energijama roditeljskih stanja Feshbach rezonance, $^1(n,3s)$ Ridbergovog stanja kod neutralnih alkohola i etera. Ova anomalija je objašnjena u ovom radu pomoću potencijalnih površina alkohola i etera, koje su računane koristeći TD-DFT metod u funkciji koordinate disocijacije. Dobijeno je da je najniže stanje alkohola odbojno, kao posledica izbegnutog presecanja $3s$ i $3p_x$ Ridbergove konfiguracije, dok kod etera postoji barijera za disocijaciju. Mešanje Ridbergovih i valentnih stanja, kao i izbegnuto presecanje, su odlučujući faktori koji definišu oblik potencijalnih površina. Zaključeno je da se reaktivnost alkohola i etera u odnosu na slobodne elektrone može racionalizovati pod pretpostavkom da potencijalne površine potomka Feshbach rezonance blisko prate ponašanje roditeljskog Ridbergovog stanja, t.j. najniža Feshbach rezonanca je odbojna ali kod etera se javlja barijera. Potencijalne površine Ridbergovog stanja i Feshbach rezonance se tako dramatično razlikuju od nedisocijativne potencijalne površine praroditeljskog $^2(n^{-1})$ pozitivnog jona, uprkos nominalno nevezivnom karakteru Ridbergovih elektrona.