

Intrinsic and extrinsic factors in anion electron-stimulated desorption: D^- from deuterated hydrocarbons condensed on Kr and water ice films

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The results of D^- ion desorption induced by 3–20 eV electrons incident on condensed CD_4 , C_2D_6 , C_3D_8 , C_2D_4 , and C_2D_2 are presented. These compounds were deposited in submonolayer amounts on the surfaces of multilayer solid films of Kr and nonporous and porous amorphous ice. While desorption of the D^- anions proceeds via well-known processes, i.e., dissociative electron attachment (DEA) and dipolar dissociation, significant perturbations of these processes due to presence of the different film substrates are observed. We have shown that it is possible to distinguish between the character and nature of these perturbations. The presence of the nonporous ice perturbs the D^- desorption intensity by affecting the intrinsic properties of the intermediate anion states through which dissociation proceeds. On the other hand, the presence of the porous ice introduces extrinsic effects, which can affect electron energy losses prior to their interaction with the hydrocarbon molecule and/or the energies and intensities of the fragment species after dissociation. Simple mechanisms responsible for the observed variations in the intensities of desorbed anionic signals are proposed and discussed. Electron transfer from transient anion states to electron states of the substrate film or nearby hydrocarbon molecules appear as the most efficient mechanism to reduce the magnitude of the DEA process. © 2004 American Institute of Physics. [DOI: 10.1063/1.1807813]

I. INTRODUCTION

The electron-stimulated desorption (ESD) of anionic species from thin multilayer molecular solids has attracted attention as a way to understand the electron-induced dissociation of condensed molecules, particularly that initiated by low-energy electrons; i.e., electrons with energies <20 eV, and involving the formation of transient negative ions (TNIs).¹ Such processes underlie a variety of phenomena related to radiation damage in biomolecules,² atmospheric reactions induced by cosmic radiation,^{3,4} surface photo-reactions,⁵ and the accumulation of charge and aging in dielectrics.⁶ The ESD of anions from thin molecular solids derives from two distinct dissociative processes, both well known from gas-phase electron-molecule scattering, dissociative electron attachment (DEA), and dipolar dissociation (DD).^{7–10} In the former case, an incident electron is temporarily captured by a molecular target to form a TNI, which decays by a dissociation into a neutral and an ionic fragment. In DD, the incident electron interaction produces an electronically excited state, which dissociates into a positively and a negatively charged fragment. In gas- and condensed-phase experiments, DEA dominates anion production for

electron-impact energies below ~ 15 eV, while the DD yield increases with electron energy above a threshold of ~ 15 eV.

In principle then, the desorption of negative ions from condensed molecules can be described in the terms adopted from the gas-phase picture. For sufficiently thick multilayer molecular films condensed onto a metallic substrate, the outermost layers are unaffected by the metal substrate and the adsorbate exists in the physisorbed state.¹¹ This weak form of adsorption is characterized by the lack of a chemical bond between the adsorbate and substrate, so that the electronic structure and vibrational frequencies of the condensed molecule are essentially unchanged from those of the gas-phase molecule.¹² Conversely, it has been shown for systems, in which a specific molecule is condensed on a multilayer molecular film condensed on a metal substrate, that the DEA and DD processes and our ability to observe them through anion desorption are strongly perturbed by the surrounding medium, i.e., the neighboring molecules and molecular solid surface.¹³ Using the nomenclature of Huels *et al.*,¹³ these perturbations can be grouped into two major classes of environmental effects, *intrinsic* and *extrinsic*. Intrinsic effects modify and perturb intermediate TNI states during DEA and the electronically excited neutral states leading to DD. In contrast, extrinsic effects influence the anion ESD process at times before the formation of the intermediate anion and after its decay. Extrinsic effects thus include the interactions of the incident electrons within the molecular film, prior to DEA or DD, and the reactions of fragment anions after dissociation.

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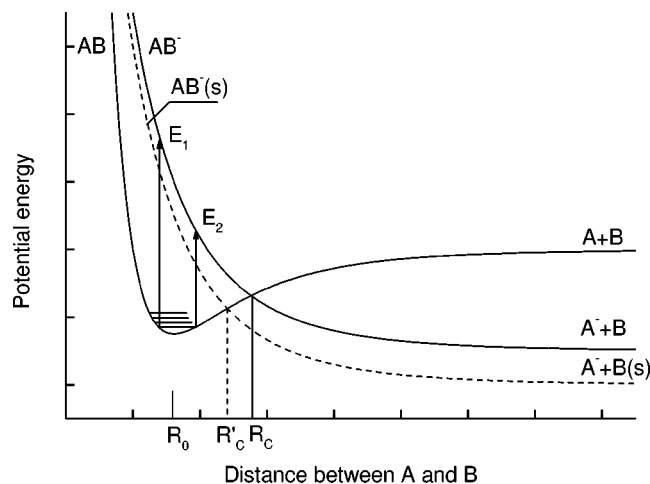


FIG. 1. Born-Oppenheimer potential-energy curves associated with dissociative electron attachment. AB represents initial potential-energy curve, where AB^- represents a dissociative anion potential-energy curve. The broken line, $AB^-(s)$, represents the potential-energy function of AB^- on the surface of a molecular solid. R_0 is the equilibrium distance of ground-state AB . AB^- is considered stable against autoionization for $R > R_C$.

II. INTRINSIC AND EXTRINSIC FACTORS IN ANION ESD

With regard to ESD via DEA, several intrinsic effects can be illustrated by considering Fig. 1, which depicts the internuclear potential-energy curves of a diatomic molecule AB and one of its TNI state AB^- ; the latter is dissociative into stable A^- and B . Assuming that only Franck-Condon transitions are possible, fragmentation of AB^- can occur with electrons of energies between E_1 and E_2 , defined by the ground-state nuclear wave function. The AB^- ion can dissociate into fragments $A^- + B$, if its lifetime is sufficiently long to survive autodetachment, which proceed for $R \leq R_C$. The negative ion is stable against autodetachment for $R \geq R_C$ since beyond this separation electron emission is endothermic. While such a treatment is only rigorously applicable for DEA to diatomic molecules, it is still qualitatively valid along a specific bond for small polyatomic molecules. Possibly, the most important intrinsic effect operating on the DEA cross section originates in the interaction between the TNI and the image charge it induces in the supporting molecular film and metal substrate.^{8,14} This surface polarization energy, E_p , lowers the potential-energy curve for AB^- by E_p relative to the gas phase, as shown by the broken curve in Fig. 1. As a result, the crossing point, R_C , moves to R'_C ; i.e., closer to R_0 . Thus, the time during which autoionization is possible becomes smaller and, consequently, the DEA cross section increases. In addition, lowering the energy of the TNI also reduces the autoionization width, so that the average autodetachment lifetime is increased and the DEA cross section is further enhanced.¹⁵ However, if for certain molecules R'_C becomes smaller than R_0 , a narrowing of the Franck-Condon region occurs, causing a decrease in both the Franck-Condon overlap and the DEA cross section.¹⁶ Obviously, the final result, i.e., increase or decrease of the DEA cross section,¹⁶⁻¹⁹ will depend on the details of the AB^- potential-energy curve and on the value of the polarization

energy. Another intrinsic effect that can either increase or decrease the desorbed signal intensity is the number of decay channels available for an autodetachment. Lowering the potential curve of the TNI reduces that number and hence increases the resonance lifetime in the condensed phase. Thus again, the DEA cross section is increased. However, on certain molecular solid surfaces, the TNI of the probed molecule and electronic states of the molecular substrate may permit electron transfer and so provide additional decay pathways for the TNI.^{20,21} In this case, autoionization may increase and the DEA cross section may decrease, with respect to that in the gas phase.

Since DD proceeds via neutral excited states of condensed molecules, perturbation by intrinsic effects is expected to be weaker than for DEA. For example, the intermediate neutral excited states of DD do not themselves induce an image charge and are thus relatively immune to the effects of polarization.²² However, both DEA and DD processes can be strongly affected by extrinsic effects. For example, below ~ 10 eV, the energy of an incident electron can be altered by scattering prior to the formation of either the DEA or DD intermediate species. Such electron energy losses represent competitive mechanisms that may reduce significantly the number of electrons of suitable energy to form the intermediate anions, so reducing molecular dissociation and the desorption signal. Alternatively, higher-energy incident electrons may inelastically scatter to an energy suitable to form intermediate anion states of lower energy.

Following dissociation, fragment anions may also interact with their environment. The presence of the image-charge-induced polarization field acts as a potential barrier to desorption and sets a minimum kinetic energy that fragment ions must possess if they are to desorb. In general, this extrinsic effect discriminates against the desorption of larger polyatomic anions due to an unfavorable partitioning of total kinetic energy during dissociation and their larger number of internal vibrational modes. Other postdissociation interactions of fragment ions include elastic and inelastic collisions with nearby atoms or molecules and a variety of ion-molecule reactions.²³ In almost all cases, postdissociation interactions reduce the kinetic energy of ionic fragments and hence reduce the ESD signal.

The influence of intrinsic and extrinsic factors on the efficiency of the ESD phenomenon has been previously studied with the O_2 molecule. Huels *et al.*¹³ found that the O^- yields per O_2 molecule are higher for O_2 deposited on rare-gas solids than on molecular solids, where the extrinsic effects of electron energy losses and postdissociation processes are much more prevalent. The weakest O^- signal was observed from O_2 on porous H_2O films deposited at 20 K. In this case, the DD signal of O^- was reduced by approximately two orders of magnitude relative to O_2 on Kr, while the O^- ESD signal from the DEA pathway was almost entirely absent. This dramatic effect (termed *quenching*) was initially attributed to an interaction of the transient O_2^- states with the dipole moment of the adjacent water molecules,²⁴ which would facilitate an electron transfer and thus reduced considerably the lifetime of the transient anion. Quenching

was therefore initially attributed to intrinsic effects. However, ice films formed at 20 K can be highly porous,^{25–27} and subsequent studies with such films of varying preparation²⁸ showed that *most* of the reduction in O^- signal was associated with the diffusion of O_2 into the porous layer. The oxygen ions formed inside the film have much lower probability of desorption than those generated at the film-vacuum interface. Nevertheless, a recent comparison of low-energy ESD from O_2 on porous ice and benzene films indicated that the marked diminution seen in the O^- yield from a water ice, particularly for DEA, was somewhat greater than could reasonably be attributed to diffusion and loss of O_2 from the film's surface alone.²⁹ Furthermore, several recent studies report electron transfer between TNI of atomic²⁰ and molecular adsorbates^{30,31} and short-lived *presolvated* electron states of water ice. These results on O_2 on ice and their interpretations illustrate the complexity of the ESD process and the difficulty to determine the factors which influence its magnitude. In the light of such work, the objective of the present study is to show that it is possible to differentiate between intrinsic and extrinsic factors influencing ESD anion yields and suggest specific mechanisms responsible for variation of the ESD intensity on environmental conditions.

III. TARGET FILMS

As a working example, we have chosen the low-energy ESD of negative ions from a number of deuterated hydrocarbons (or *deuterocarbons*) deposited onto a clean platinum foil and multilayers of Kr and H_2O of varying preparation. The deuterocarbons include the saturated molecules CD_4 , C_2D_6 , and C_3D_8 , and unsaturated C_2D_4 and C_2D_2 . Since it was shown that the desorbed yield of negative ions from molecules condensed on ice films can strongly depend on their porosity (e.g., Refs. 28, 29, and 32), the deuterocarbons are condensed on porous and nonporous amorphous ice to determine the effect of morphology. The use of deuterated compounds permits us to discriminate between anion yields from ice and the molecular adsorbate.

Rare-gas solids provide an almost perfectly inert host surface, since only phonons of low energy can be created from particle interactions in these solids below their electronic excitation thresholds. The number and efficiency of extrinsic processes affecting ESD in rare-gas solids are therefore very small; e.g., much smaller than for polyatomic molecular solids, as shown in studies of DEA, to O_2 condensed on rare solid films^{8,22} and other substrates.¹³ From these considerations, perturbation of TNI states due to intrinsic effects is also expected to be small for molecules adsorbed onto a krypton spacer film. The most important intrinsic effect connected with a krypton multilayer substrate is an anionic exciton transfer process,^{33–35} i.e., creation of an electron-exciton complex in Kr substrate, which transfers electron and energy to a condensed molecule. The intrinsic effect of transfer can be easily distinguished as a sharp resonance peak near 9.7 eV superimposed onto a much broader regular resonance maximum. Considering that extrinsic effects due to presence of the Kr substrate for the studied targets should give at least very similar perturbations of the recorded intensities, we treat yield functions of negative anions from deu-

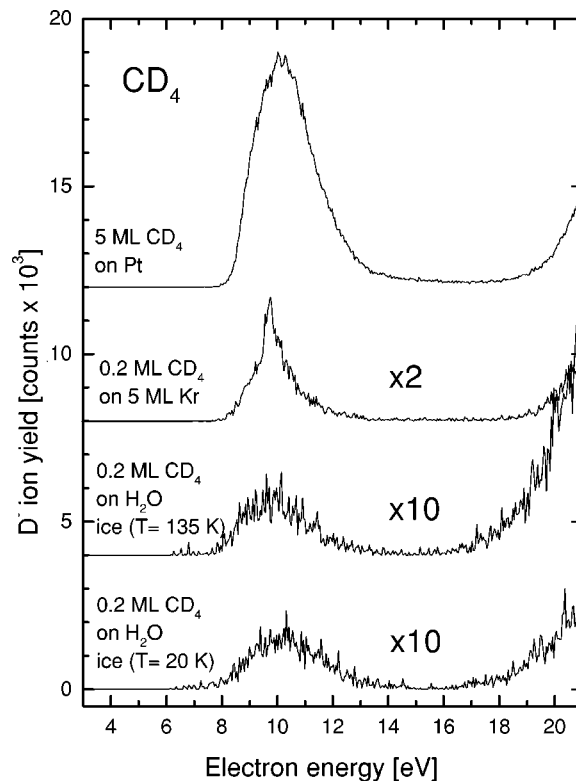


FIG. 2. D^- ion yield functions from electron impact on CD_4 molecules condensed onto Pt, Kr, and porous ($T=20$ K) and nonporous ($T=135$ K) ice films.

terocarbons condensed onto a krypton spacer film as a reference signal. In other words, when contributions to the anion yield originating from intrinsic effects due to the creation of electron-exciton complex are excluded, the desorption signal from the Kr surface is considered free from intrinsic and extrinsic effects.

Previous experimental investigations of anion ESD from hydrocarbons and corresponding deuterocarbons have dealt with the desorption of H^- , CH^- , CH_2^- , and CH_3^- by low-energy (5–20 eV) electron impact on simple saturated (C_nH_{2n+2} , $n=1-9$) and unsaturated (C_nH_{2n} , $n=2-4$) hydrocarbons condensed onto Pt.^{36,37} D^- anion desorption yields have been measured for four monolayers (ML) films of C_2D_4 , C_2D_6 , and C_6D_6 molecules condensed onto Pt, as well as C_2D_4/H_2O , C_2D_6/Ar , C_2D_6/Kr , C_2D_6/Xe , C_6D_6/Ar , C_6D_6/Kr , and C_6D_6/Xe systems.^{13,33} Recently, we have reported D^- ion desorption due to electron impact on CD_4 , C_2D_2 , C_2D_4 , C_2D_6 , and C_3D_8 condensed onto a polycrystalline platinum surface.³⁸

IV. EXPERIMENT

The apparatus employed in the present experiments has been described in detail elsewhere.¹³ Briefly, it consists of an electron hemispherical monochromator producing an 80-meV full width at half maximum (FWHM) electron beam, a cryogenically cooled target, and a quadrupole mass spectrometer. These are housed within an ultrahigh-vacuum chamber maintained at a background pressure of 10^{-10} Torr by a combination of an ion pump and a closed-cycle refrig-

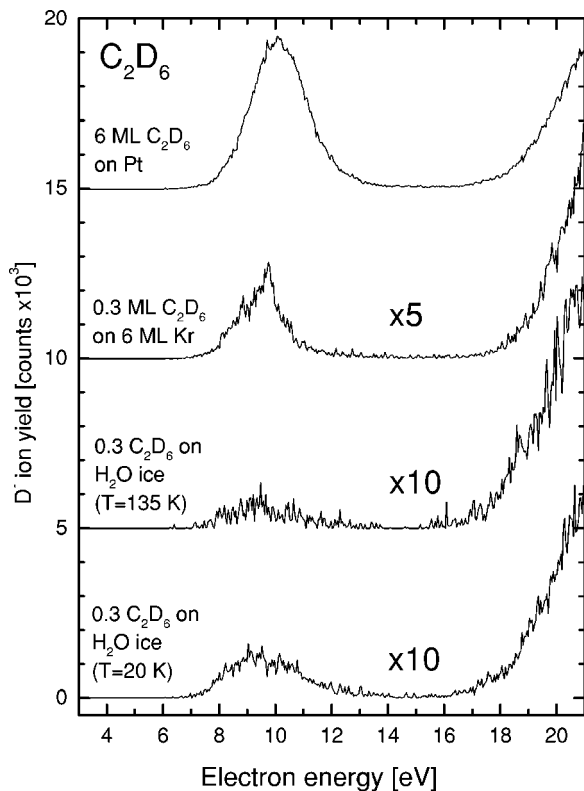


FIG. 3. D^- ion yield functions from electron impact on C_2D_6 molecules condensed onto Pt, Kr, and porous ($T=20$ K) and nonporous ($T=135$ K) ice films.

erated cryopump. The residual magnetic field in the region of the electron and ion optics and at the electron monochromator and interaction region is reduced to less than 15 mGauss with a double μ -metal shield.

Multilayer atomic and molecular films are condensed onto a clean, electrically isolated polycrystalline (0.007 in.) platinum foil press fitted to the tip of the closed-cycle He cryostat. The angle of the axis of the dosing nozzle is $\sim 45^\circ$, with respect to the Pt surface normal. The foil may be cleaned by resistive heating to approximately 900 K. Its minimal operating temperature of 20 K is well below the sublimation point of all the substances investigated. In the present experiment, the rare-gas solid films were grown at 20 K, whereas the H_2O spacer layers were grown at temperatures ranging between 20 to 140 K. The latter were prepared from a H_2O sample that was distilled and subjected to a number of freeze-pump-thaw cycles before deposition. The porous amorphous water ice films^{39,40} have been grown by direct water-vapor deposition onto the Pt foil at 20 K, whereas nonporous amorphous water ice films⁴¹ have been obtained in two ways, by direct water deposition onto Pt foil at 135 K and/or by gradually warming and annealing of the porous films to 135 K. In each case, water films were cooled to 20 K prior to the deposition of the deuterocarbons. The ESD yields were always recorded at 20 K. The thicknesses of the ice and rare-gas solid films were determined in ML by a volumetric dosing procedure⁴² with an uncertainty of no more than 50% and a reproducibility of about 0.2 ML. While the very small amounts of the deuterocarbons condensed on

the H_2O and Kr spacer films (0.2 ML) could have an absolute uncertainty of as large as 50%–100%, the relative ESD intensities presented here are reproducible, such that differences in intensities observed on different substrates have a physical basis. Pure sample gases from Cambridge Isotope Laboratories were used with a stated minimum isotopic purity of 99% for deuterated methane (CD_4) and acetylene (C_2D_2), and 98% in the cases of deuterated ethylene (C_2D_4), ethane (C_2D_6), and propane (C_3D_8). Krypton solid films were grown from krypton gas with a stated purity of 99.995%.

The thin films were bombarded with a 0–20 eV electron beam of about 1 nA current produced by the monochromator. The beam was incident on the target surface at an angle of 70° to the normal and its absolute energy scale was determined to within ± 0.3 eV with respect to the vacuum level, by observing the onset of current transmission to the platinum metal as a function of electron energy. The desorbed anions were collected with electrostatic lenses and mass-selected with a quadrupole mass spectrometer positioned at 20° from the surface normal. Ions were detected with an electron multiplier. The mass spectrometer and ion optics have an acceptance angle of 25° . Measurements of the ESD of anions, as a function of incident electron energy, are termed as “ion yield functions.”

V. RESULTS AND DISCUSSION

A. D^- desorption from deuterocarbons condensed onto Kr and nonporous and porous water ice films

The ion yield functions of the deuterocarbons CD_4 , C_2D_6 , C_3D_8 , C_2D_4 , and C_2D_2 are reported in Figs. 2–6, respectively. Each figure contains the D^- ion yield functions from submonolayer quantities of the studied molecules adsorbed onto Kr, nonporous ice and porous ice films. Additionally, for a comparison in each figure, a D^- yield function from a pure multilayer film of the corresponding molecule is plotted. The energies of these broad resonant features and their FWHM are listed in Table I. The low count rates obtained in the present experiment have required that some of the data be represented as the sum of several yield functions; in these cases, care was taken to minimize the effects of charge trapping^{1,6} by preparing new films as necessary.

All D^- yield functions display a threshold near 7 eV and a single strong broad resonant maximum. For deuterocarbons condensed onto the krypton substrate, this resonant feature is centered around 9.8 eV for CD_4 and C_2D_4 , 9.5 eV for C_2D_6 , and near 9 eV for C_2D_2 and C_3D_8 . When these molecules are condensed onto nonporous ice films, the D^- yield signal from C_2D_6 and C_2D_4 is peaked at the same energies as seen on Kr. The position of the maximum is shifted to 10.2 eV for CD_4 , 9.2 eV for C_3D_8 , and 9.4 eV for C_2D_2 . In general, these energies remain unchanged when the deuterocarbons are deposited onto porous ice films, except for C_2D_2 , where the resonant maximum is shifted down to 8.7 eV. In all cases, the broad resonantlike structure is attributed to D^- abstraction via DEA, i.e.,

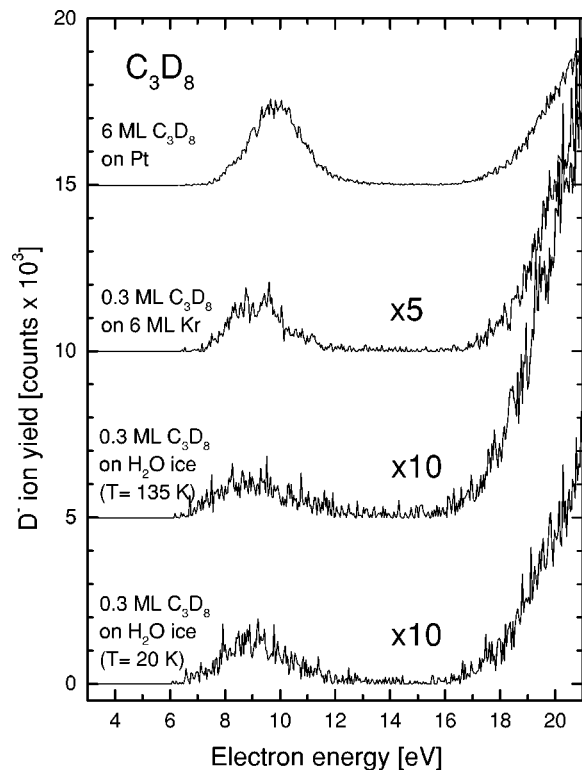
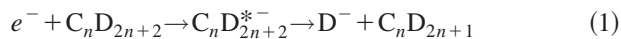
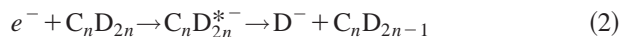


FIG. 4. D^- ion yield functions from electron impact on C_3D_8 molecules condensed onto Pt, Kr, and porous ($T=20$ K) and nonporous ($T=135$ K) ice films.



and



for saturated and unsaturated compounds, respectively. This process is thought to involve the dissociation of core-excited TNIs of Rydberg character, which are created when an incident electron is captured into an empty orbital of σ^* symmetry.³⁷ For deuterated acetylene (C_2D_2) deposited on Kr and on nonporous and porous ice substrates, the D^- yield functions clearly show at 12 eV an additional broad peak. There is also some evidence in the case of C_2D_2 on Kr, at 15 eV for the presence of a weak resonantlike structure. Observations of these two additional structures at 12 and 15 eV have been reported previously for pure films of deuterated acetylene³⁸ and have tentatively been assigned to higher-lying Feshbach resonances of Rydberg character.^{43,44} Since the present results are obtained with very low surface coverage of C_2D_2 , they support the attribution of these structures as arising from direct DEA rather than from DEA following energy losses by higher-energy electrons.

The D^- yield functions for submonolayer quantities of the saturated compounds condensed on krypton display a relatively sharp peak in the vicinity of 9.7 eV, i.e., just below the energy of the lowest electronic transition in solid Kr. This enhancement is superimposed onto a broader resonant peak similar to that seen for the pure films. It is due to electron-exciton complex formation in the Kr substrate and its transfer to the hydrocarbon adsorbate,³³⁻³⁵ as described previously.

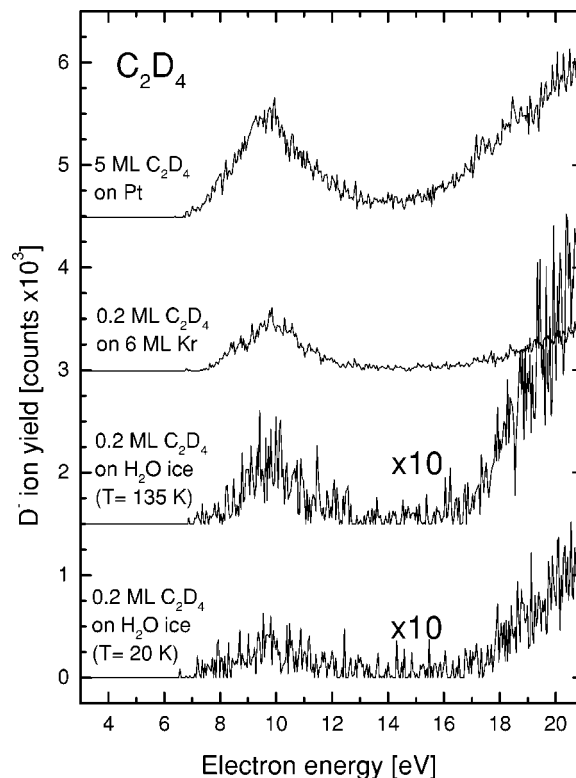


FIG. 5. D^- ion yield functions from electron impact on C_2D_4 molecules condensed onto Pt, Kr, and porous ($T=20$ K) and nonporous ($T=135$ K) ice films.

A similar behavior in the ESD signal of anions from condensed molecules on rare-gas solids has been observed for D^-/D_2O (Ref. 45), D^-/C_2D_6 (Ref. 33), O^-/CO_2 (Ref. 46), F^-/SF_6 (Ref. 47), $Cl^-/CFCl_3$ (Ref. 48), and Cl^-/CF_2Cl_2 (Ref. 49). Surprisingly, for the unsaturated deuterocarbons, i.e., C_2D_2 and C_2D_4 , the narrow Kr^{*+} feature is absent from the D^- yield functions. Since significant Rydberg character of the intermediate molecular anion state is required for such coupling,³³ it indicates that coupling of the electron-exciton complex to the molecular anion states of unsaturated deuterocarbons is inefficient or that the transfer occurs for anions states, where decay channels are not observed in our experiments. In fact, gas-phase experiments⁵⁰⁻⁵² indicate that H^- formation due to DEA to C_2H_2 represents only one of several competing decay channel for Rydberg resonant states. C_2^- production is even ten times more intense than that for H^- .⁵¹ Similarly, the C_2H_4 Rydberg resonant states can either produce C_2H^- , CH^- , or H^- .⁵¹ Again, the intensity of the H^- signal is lower than that for C_2H^- .⁵¹ In contrast, the H^- decay channel for saturated hydrocarbons is the most probable.⁵¹ Thus, it is possible that even if the transfer from the exciton complex to the TNI states of unsaturated deuterocarbons occurs, it is mainly present in the channel that promotes decay to polyatomic negative fragments, which do not escape the surface.

Above 15 eV for C_2D_4 , 17 eV for C_2D_2 , C_2D_6 , and C_3D_8 , and 19 eV for CD_4 , the ion yield is observed to increase linearly with the incident electron energy indicating the involvement of the direct DD process.

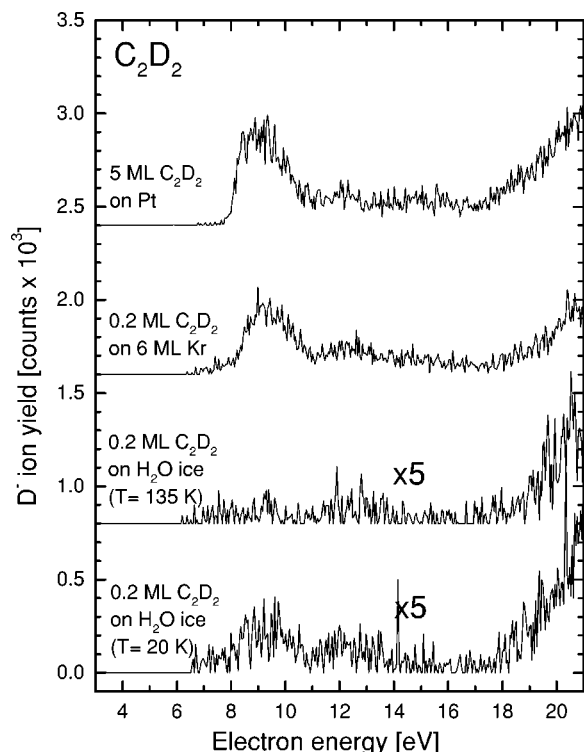


FIG. 6. D^- ion yield functions from electron impact on C_2D_2 molecules condensed onto Pt, Kr, and porous ($T=20$ K) and nonporous ($T=135$ K) ice films.

B. Perturbation of ESD due to intrinsic and extrinsic effects

Using the data of Figs. 2–6, Table II reports the intensities of the D^- signal from submonolayer quantities of each deuterocarbon, condensed on nonporous and porous ice, relative to that generated from the same quantity condensed on Kr. To reduce the effects of low count rates, the ESD signal has been integrated over two energy ranges that correspond approximately to the two mechanistic components contributing to this signal; one between 5 and 15 eV, associated with DEA, and another between 15 and 21 eV, associated with DD. Organizing the data in this manner allows certain arguments to be developed.

1. Diffusion in porous and nonporous ice films

It is easily apparent from Figs. 2–6 and Table II that for each of the studied molecules, the ESD yield of anions

changes only subtly with a different substrate from nonporous ice and porous ice, and that these yields are essentially of the same order. This is in contrast with results for O_2 on porous and nonporous ice,²⁸ where the comparative weakness of the signal on porous ice was shown to derive essentially from the diffusion of O_2 into the supporting molecular solid. However, it was previously shown by infrared spectroscopic measurements that such diffusion is a thermally activated process; deposited molecules will remain on the surface of a porous ice film until the temperature of the film is raised above a certain value, characteristic of the deposited molecule.⁵³ This value is typically several degree Kelvin lower than the sublimation temperature of these molecules. Deuterated methane is the lightest molecule studied in the present experiment and should have the lowest activation temperature for diffusion. Yet, it shows no obvious signs of disappearance from the film/vacuum interface. It seems likely then that for each of the studied molecules, diffusion of the deuterocarbon species into the porous ice network is severely limited and can be neglected for molecules adsorbed on the denser nonporous ice surface.

2. Nonporous ice

Inspection of Table II shows that for both CD_4 and C_3D_8 on nonporous ice, the DD signal is within 5% the same as that observed when these molecules are condensed on Kr. Such a situation arises if the intrinsic and extrinsic effects relevant to DD were similar on ice and Kr, or if fortuitously, any increase in extrinsic effects for nonporous ice were offset by changes in intrinsic factors. Clearly, the former case seems much more plausible, so we consider that the extrinsic effects on DD for these molecules are at the same low levels on nonporous ice as they are when adsorbed on Kr. As a consequence, we must conclude that the intrinsic effects on DD are at similar levels in the case of the Kr and nonporous ice substrates and are therefore negligible. Furthermore, it seems reasonable that a similar situation pertains to the saturated molecule of intermediate size C_2D_6 , and that the lower ratio, .81, in Table II reflects the uncertainty in the measurement. The three saturated molecules share similar electronic structure, so if extrinsic effects are negligible for CD_4 and C_3D_8 , they would also be very small for C_2D_6 . Thus, we conclude that, essentially, no intrinsic and extrinsic effects perturb the dipolar dissociation process for saturated molecules condensed onto nonporous ice.

TABLE I. Resonance energies and DEA peak width (in eV) for D^- anions desorbed by electron impact from deuterated hydrocarbon molecules condensed on a Pt substrate and Kr and ice films.

Parent molecule	Platinum		Krypton ^a		H ₂ O ($T=20$ K)		H ₂ O ($T=135$ K)	
	Energy	FWHM	Energy	FWHM	Energy	FWHM	Energy	FWHM
CD_4	10.1	2.5	9.8	1.1	10.2	3.0	10.1	2.8
C_2D_6	10.0	2.3	9.5	2.0	9.5	3.0	9.5	2.5
C_3D_8	9.9	2.3	9.0	2.1	9.2	2.6	9.2	3.0
C_2D_4	9.7	3.1	9.8	2.6	9.8	2.8	9.8	3.0
C_2D_2	9.2	1.9	9.1	1.8	9.4	2.9	8.7	2.5

^aThe peak widths refer to regular broad resonant structures and enhancement due to electron/excimer complex is excluded.

TABLE II. Ratio of desorption signal intensities from deuterocarbons condensed onto ice and Kr substrates. The ESD signal is broken into DEA and DD components.

Molecule	Non-porous	Non-porous	Δ DD/ Δ DEA	Porous	Porous	Δ DD/ Δ DEA
	Ice/Kr DEA	Ice/Kr DD		Ice/Kr DEA	Ice/Kr DD	
CD ₄	0.20	0.97	4.9	0.20	0.40	2
C ₂ D ₆	0.21	0.81	3.9	0.43	0.60	1.4
C ₃ D ₈	0.52	0.95	1.8	0.54	0.50	0.9
C ₂ D ₄	0.14	0.58	4.1	0.09	0.25	2.8
C ₂ D ₂	0.081	0.25	3.1	0.17	0.34	2

Recalling that extrinsic factors affect both the energies of incident electrons and the desorption probabilities of dissociated fragment ions, it is likely that for the saturated molecules on nonporous ice, extrinsic effects will also be absent from the DEA component to the ESD signal. For example, recent cross-section measurements for electron scattering in ice⁵⁴ show that below 20 eV, the dominant energy-loss process (with cross sections of $\sim 10^{-17}$ cm²) are associated with vibrational modes of excitation, which will reduce only slightly the energy of incident electrons. In contrast, the combined cross sections for DEA, electronic excitation and ionization, processes that can drastically affect electron energy are one to two orders smaller. Thus, for the thin (4 ML) nonporous ice films used in these experiments, there is no reason to believe that the energies of incident electrons would be more strongly perturbed at the low energies (5–15 eV) of DEA than at the higher energies required for DD. Similarly, in previous investigations of anion desorption from various hydrocarbons deposited on Kr,⁵⁵ the kinetic-energy distributions of desorbed H⁻ from DEA and DD processes were found to be much alike. Under these conditions and considering the absence of extrinsic effects for DD, the substantial reduction in intensity of the DEA signal (i.e., the integrated ESD signal from 5 to 15 eV) for CD₄, C₂D₆, and C₃D₈ condensed on nonporous ice must be due to intrinsic effects. This decrease in the DEA signal could derive from a transfer of the excess electron from a deuterocarbon anion into an electron state of (H₂O)_n within the film.²⁰ Moreover, it is likely that even at these low coverages, hydrophobic deuterocarbon molecules cluster on the nonporous water substrate and are poorly isolated from one another. Such a situation would increase the probability of electron transfer from one deuterocarbon anion to another, which would have the effect of reducing the lifetime of the TNI on each molecule and hence the DEA yield of anions.

For the unsaturated deuterocarbons (i.e., C₂D₄ and C₂D₂) condensed onto the nonporous ice film, the DD-linked desorption yield decreases by factors of 2 and 4, respectively, relative to those observed with a Kr substrate. These molecules on nonporous amorphous ice films are randomly oriented, as in the case of the saturated deuterocarbons. Hence, the overall distribution of kinetic energy and desorption angles of anions arising from C₂D₄ and C₂D₂ will be similar to those for saturated deuterocarbons. Thus, the absence of extrinsic effects modulating D⁻ desorption from the saturated compounds suggests they will likewise not affect the DD and DEA yields from condensed C₂D₄ and C₂D₂ mol-

ecules. Therefore, the observed decrease in DD and DEA intensities for these molecules is expected to be related to intrinsic effects. Since DD proceeds via a neutral excited state, it is possible that π^* states, which lie in the ionization continuum, autoionize before dissociation, particularly, since their dissociative potential-energy surfaces are not as steep as those of the σ^* bonds. Alternatively, it is entirely possible that transitions from π^* states into the DD intermediate state are less favorable than from σ^* states. If π^* excitation of the unsaturated molecules decreases the probability of forming a σ^* excitation, then the yield of ions by DD would also be expected to fall.

The decrease in the anion yield from the DEA intensity for unsaturated deuterocarbons is interpreted as in the case of the saturated molecules, i.e., as a result of the transfer of the excess electron from C₂D₄^{*-} and C₂D₂^{*-} to an electron state of the water substrate or neighboring deuterocarbon molecules. In passing, we note that for the unsaturated compounds, the drop in the DEA-related anion signal (by factors of 7 and 12 for C₂D₄ and C₂D₂, respectively) from intrinsic effects is greater than that seen for DD component. Remembering that these two intrinsic effects are different from each other and thus can suppress the desorption signals differently, this latter observation provides a demonstration that the anionic intermediate state in DEA is more easily and strongly perturbed than the intermediate neutral excited state in DD, as was argued in Sec. I.

3. Porous ice films

Unlike experiments with the nonporous ice films, the intensity of the DD-related yields from the saturated deuterocarbon molecules on porous ice substrate are a factor of 2 weaker than for the same molecules on Kr. Since in the present experiments, both the nonporous and porous ice surfaces are amorphous, the lack of intrinsic modulations on the DD-related signal for saturated deuterocarbons deposited onto the nonporous ice surface implies that intrinsic effects remain unimportant for DD of these molecules on porous ice. Thus, the observed reduction should be due to extrinsic effects. Even if as argued earlier, the diffusion of deuterocarbons into the porous ice film is limited, the porous ice surface is more uneven and rougher than the nonporous surface. Thus, more postdissociation events (e.g., ion scattering) are expected to occur and could easily explain the observed suppression of desorbed signal. The same will also be true for C₂D₄, where an additional reduction in DD signal from this

molecule derives from the intrinsic effect of π bonding as is the case for its adsorption onto nonporous ice films.

The extrinsic effect of the ice film porosity should also be expected to reduce the DEA-related desorption yields. Nevertheless, it is clear from Table II that the reduction in DEA signal by deposition onto porous ice (excepting C_2D_2) is the same or smaller than with nonporous ice. Taking into account the reduction in desorption due to postdissociation extrinsic effects, which should reduce the DEA-related signal by a factor of about 2, it is clear that intrinsic effects are less intense on porous ice than on nonporous ice, for each of the studied deuterocarbons. In the case of the C_2D_2 molecules adsorbed onto porous ice, it seems that a suppression of intrinsic effects is even greater than for other deuterocarbons. It should be considered, however, that the rough surface of the porous water ice film has a larger area than the smoother nonporous ice surface. This condition reduces the probability that the deposited deuterocarbon molecules touch or form clusters on the surface of the ice film. Such a situation would limit intermolecular electron transfer, increase the lifetime of the TNI, and hence the probability of its dissociation.

VI. CONCLUSIONS

As with many molecules, low-energy electron impact onto small quantities (0.2 ML) of the deuterocarbons CD_4 , C_2D_6 , C_3D_8 , C_2D_4 , and C_2D_2 condensed onto Kr and nonporous and porous water ice substrates stimulates the desorption of D^- ions via DEA (near 10 eV) and DD (above ~ 15 eV). On Kr films, the D^- yield functions from the saturated deuterocarbons additionally exhibit a strong and sharp resonant peak at 9.7 eV from coupling between the transient anion states of the deuterocarbons and the electron-exciton complex of the Kr substrate. No such coupling is observed for the unsaturated molecules, possibly from the weaker Rydberg character in the transient anion states of these molecules.

From a detailed analysis and comparison of the signal obtained from these deuterocarbons adsorbed on Kr and ice surfaces, we have shown that it is possible to distinguish between intrinsic and extrinsic factors affecting the ESD of anions. We observed that perturbations of the ESD process from saturated and unsaturated deuterocarbons deposited onto nonporous ice substrates have only an intrinsic character. This result will hold true for other molecules producing D^- (or H^-) of similar kinetic energies, by DEA or DD at comparable incident electron energies. In the absence of reactive ion scattering or other postdissociation interactions, it will also apply more generally to the ESD of different anions from other molecular targets. When modulated by intrinsic effects, anion ESD will be highly dependent on the electronic structure of the target molecule. Here, we attribute a reduction in the DEA component to desorption from these molecules on nonporous ice, relative to Kr, to a transfer of the excess electron from the deuterocarbon anion to either an electron state of $(H_2O)_n$ in the film or on a neighboring molecule. Similarly, a comparative reduction in the DD component of the ESD signal from unsaturated deuterocarbons on nonporous ice is taken as due to intrinsic modulation of the autoionization of neutral excited state prior to dissociation.

Increasing the porosity of the ice substrate introduces extrinsic effects connected with postdissociation interaction (e.g., ion scattering), which suppresses the DEA and DD signals by a factor of 2 relative to nonporous ice. Once more, such a result can be expected for other molecules deposited onto these substrates. Note however, that for these comparatively large molecules deposited at temperatures well below their sublimation points, the extrinsic effects of porosity are considerably less than were observed for O_2 ,²⁸ which more easily diffuses into a porous water film. In general then, film porosity may not be as an important factor in these types of ESD experiments as previously assumed. Finally, we suggest that the intrinsic effect of electron transfer between TNIs of neighboring deuterocarbons is weaker than for nonporous ice since deuterocarbons on the rough porous surface remain more isolated from each other.

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