

Optical spectra of two-dimensional butadiene iron tricarbonyl in the adsorbed state

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We use optical remission spectroscopy to investigate the orientation of physisorbed $C_4H_6Fe(CO)_3$ [butadiene iron tricarbonyl (BIT)] with respect to the surface of a boron nitride substrate. Remission spectroscopy reveals a structured spectrum in the uv-visible spectral range consisting of several distinct bands. The energy positions and relative intensities of these bands can be utilized to describe the orientation of the BIT molecules relative to the substrate surface. To this end we perform complete neglect of differential overlap model calculations on the basis of two preferential orientations. The BIT molecule is assumed to be oriented either with its three CO ligands (BIT-I) or with its butadiene ligand (BIT-II) towards the substrate surface. Comparison of the calculated results with the experimental spectrum suggests that the molecule assumes the BIT-II configuration when adsorbed on boron nitride.

I. INTRODUCTION

Adsorbed films have interesting properties. The phenomena observed in these systems are important with respect to practical application as well as to basic research: One field of interest is heterogeneous catalysis at surfaces; another is the study of phase transitions in two dimensions. Depending on the strength of the interaction between an adsorbed molecule and the substrate, molecule-substrate bonding and/or intermolecular lateral interactions determine the behavior of the adsorbate. Adsorbate overlayers with weak molecule-substrate interaction (physisorbed overlayers) very often show a behavior similar to that of quasi-two-dimensional (2D) systems. The phase transition from the 2D solid to the 2D liquid phase of such 2D systems has gained increasing interest in recent years in connection with theoretical investigations of the melting phase transition in plane (2D) systems (refer to the Kosterlitz-Thouless theory and related dislocation theories¹). A great variety of spectroscopic methods, including x-ray and ultraviolet photoelectronic spectroscopy, low-energy electron diffraction and electron-energy-loss spectroscopy, and ion scattering,² have been applied to investigate the electronic and geometric structure of molecules adsorbed on various substrates. Neutron,³ x-ray,⁴ and Mössbauer scattering,⁵ as well as calorimetric⁶ and volumetric⁷ methods have been extensively applied as well to study 2D phase transitions.

Optical methods have so far received little attention to study such problems. Only very recently has it been possible to observe the 2D melting transition of butadiene iron tricarbonyl [$C_4H_6Fe(CO)_3$ (BIT)] adsorbed on hexagonal boron nitride (BN) using remission spectroscopy.⁸ This spectroscopic method is based on the pioneering work of Kortüm.⁹ It is especially suitable for the study of the optical spectra of powders and films adsorbed on such powders. When the spectra of adsorbed films are to be in-

vestigated, then the powder substrate should have a spectrum approximately flat in the spectral range of interest. The remission method allows one to deduce information on both the phase transitions within the adsorbed film via a change of the light-scattering coefficient as a function of temperature and also the absorption spectra of the adsorbed species. The BIT molecule investigated in the present work is suitable for such optical remission experiments because the molecule absorbs light in the uv-visible region which is a necessary condition for doing optical spectroscopic investigations of phase transitions.

In a previous paper¹⁰ the change of the scattering coefficient of light of the adsorbed BIT molecules as a function of temperature was discussed in detail. This aspect is important for the study of the melting phase transition of BIT. In the present paper we concentrate on an analysis of the absorption coefficient of adsorbed BIT which gives information about the alteration of the molecular electronic states due to absorption. On the basis of numerical model calculations we discuss the modification of the electronic structure of BIT where we assume two possible geometric orientations relative to the substrate. One can think of the BIT molecule as being oriented either with its three CO ligands or with the butadiene ligand towards the substrate. For the latter specific orientation we find a BIT absorption spectrum that is substantially different from the absorption spectrum of the free (nonadsorbed) BIT molecule. This change can be attributed to the interaction of the molecule with the BN substrate.

The present paper is organized as follows. In Sec. II we will briefly discuss the spectroscopic experiment and technical details of calculating the spectrum. Section III contains a summary of the electronic properties of the free BIT molecule. In Sec. IV we discuss the experimental and theoretical results for BIT in the adsorbed state and compare the properties of free and adsorbed BIT. Finally, we present a conclusion.

II. EXPERIMENTAL AND CALCULATIONAL DETAILS

The experimental setup has been described in detail in the previous paper.¹⁰ We mention that the sample holder for housing the substrate was inside a high-vacuum chamber mounted on a cold finger (cooled to about 100 K). We used a commercial Beckman spectrometer model No. UV 5240, extended by a system of five additional toroidal and plane mirrors to lead the light beam to the substrate pellet in the vacuum chamber and after remission back to the detector of the spectrometer. The substrate consisted of commercially available BN (grain size 1–5 μm) cleaned under high-vacuum conditions (10^{-5} mbar) prior to adsorbing BIT films. The remission spectrum of the adsorbed film is represented by its spectral intensity $J(R_{\text{film}})$. For a "white" substrate like BN (energy gap 41 000 cm^{-1} at the boundaries of the Brillouin zone), loaded with a weakly absorbing film, $J(R_{\text{film}})$ assumes the simple form (for details see Refs. 8 and 10)

$$J(R_{\text{film}}) = \kappa_{\text{film}} / (s_{\text{sub}} + s_{\text{film}}) \quad (1)$$

R_{film} is the reflectivity due to the film, κ_{film} the absorption coefficient, and s_{film} the scattering coefficient. $J(R_{\text{film}})$ is also called the Kubelka-Munk function.⁹ As stated in the Introduction, we are mostly interested in the parameter κ_{film} and the consequences of its wavelength dependence in the present paper, while the properties of the scattering coefficient s_{film} have been discussed in detail in the previous paper.¹⁰

A BIT film of a given density was prepared by evaporating a defined amount of liquid BIT into the vacuum chamber. During adsorption the BN substrate was maintained at 120 K. A BIT film prepared in such a way tends to cluster rather than forming a smooth layer. By keeping the adsorbed film at 200–220 K for many hours and thereby tempering the film, however, we can reach a homogeneous quasi-two-dimensional distribution of BIT molecules on the surface. To monitor the actual film state during tempering the remission spectra were recorded until a steady state of the film was reached.

The calculations upon which the interpretation of the experimental results is based, will be described in Sec. IV, and are done with the semiempirical complete neglect of differential overlap (CNDO) self-consistent-field (SCF) algorithm, described in detail elsewhere.¹¹ The principle idea is that first the many-electron problem is self-consistently solved in the single-particle approximation. This procedure results in the SCF ground states. From the SCF determinant we create excited configurations by redistributing the electrons among the occupied and unoccupied SCF one-electron states. On this basis the correlated wave functions for ground and excited states are determined by configuration interaction including doubly excited configurations.

III. ELECTRONIC PROPERTIES AND SPECTRUM OF THE FREE BIT MOLECULE

Next, we give a short review of the electronic properties of the free (nonadsorbed) BIT molecule. The molecule can be imagined to be made up of a butadiene ligand

which via its π orbitals is bound to an $\text{Fe}(\text{CO})_3$ fragment. Figure 1 shows how the interaction between the two parts can be visualized within a molecular orbital scheme.^{12,13}

The π orbitals of the butadiene molecule are shown on the right-hand side of Fig. 1. They consist of the occupied orbitals π_1, π_2 and the empty orbitals π_3, π_4 . According to the C_s symmetry of the BIT molecule (not the C_{2v} symmetry of planar *trans*-butadiene) the π orbitals are classified as symmetrical and antisymmetrical. On the left-hand side of the figure the highest occupied orbitals of $\text{Fe}(\text{CO})_3$ are shown. They are labeled $1a_1^{(s)}$, $1e^{(s,a)}$, and $2e^{(s,a)}$ followed by the empty orbital labeled $2a_1^{(s)}$. The shapes of these orbitals indicate that they have been generated by the superposition of s , p , and d orbitals on the Fe atom. If the initially separated butadiene ligand and the $\text{Fe}(\text{CO})_3$ fragment are allowed to interact, orbitals of equal symmetry will overlap and split depending on their mutual energetic distance. Common energy levels are formed. The most efficient interactions appear between the orbitals $2e^{(a)}$ and π_2 as well as between $2e^{(s)}$ and π_3 . A smaller interaction is observed between $1a_1^{(s)}$ and π_1 , whereas the energetic position of $1e^{(s,a)}$, because of very

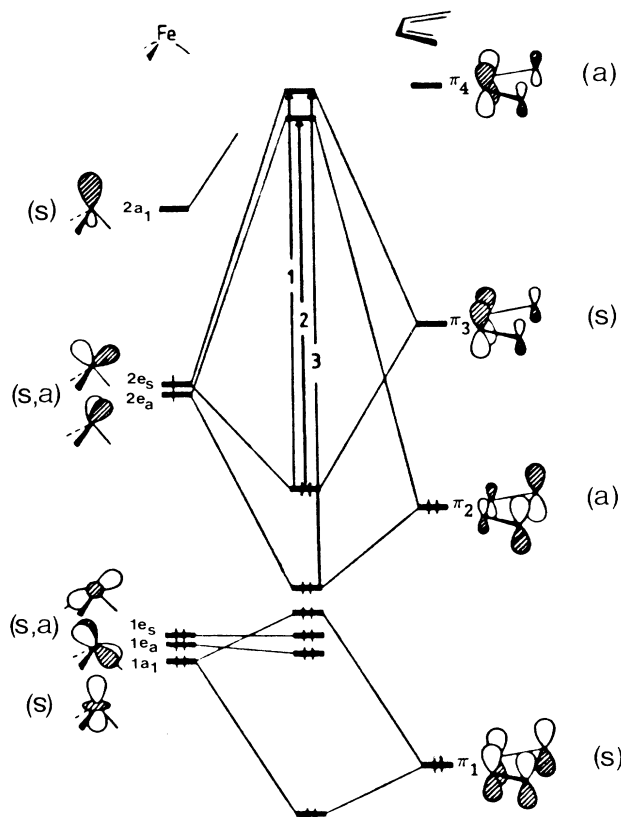


FIG. 1. Molecular orbital scheme for the free BIT molecule (middle part of the figure) (Ref. 12). Left-hand part: iron orbitals of the $\text{Fe}(\text{CO})_3$ fragment; right-hand part: butadiene fragment. The energy levels in the middle of the figure arise when both fragments come to interact with each other. The transitions labeled by arrows 1, 2, and 3 correspond to the calculated energies of 29 200, 42 700, and 43 500 cm^{-1} , respectively (refer to Table I and the discussion in text).

small overlap, nearly does not move. We therefore anticipate that the optical absorption spectrum will be dominated by the transitions 1, 2, and 3 (Fig. 1) in the low-energy regime involving iron and butadiene orbitals. Transitions involving the CO ligands, however, should be expected at elevated energies.

Table I compares the experimental^{14,15} with the calculated spectrum. The calculated peak positions are accompanied by their oscillator strengths f which determine the peak intensities. The first transition is of low intensity experimentally as well as theoretically ($f = 4.4 \times 10^{-3}$). It is situated experimentally (inset of Fig. 2) at $28\,000\text{ cm}^{-1}$ and calculated to be $29\,200\text{ cm}^{-1}$. The second absorption line is of fairly high intensity which also is in agreement with calculation ($f = 1 \times 10^{-1}$). It is observed experimentally (Fig. 2) at $36\,000\text{ cm}^{-1}$ and calculated at $42\,700\text{ cm}^{-1}$. Therefore, experimental and calculated spectral parameters behave consistently.

If one decomposes the calculated many-particle transitions into those between single-particle states, 80% of the transition at $29\,200\text{ cm}^{-1}$ appears to originate from states which have considerable iron d character. This explains the low intensity (small f), as $d \rightarrow d$ transitions are forbidden because of angular momentum conservation. The transition at $42\,700\text{ cm}^{-1}$ contains contributions from an $\text{Fe} \rightarrow \pi$ butadiene transition of 60%. This explains its large f .

It is known that CNDO-SCF calculations on organic molecules with π electrons often overestimate electronic excitation energies when the standard CNDO parametrization is used.¹¹ We therefore expect an overestimation of those electronic transitions which involve butadiene orbitals, while in accordance with calculations on $\text{Fe}(\text{CO})_5$, using the present method, excitations on the $\text{Fe}(\text{CO})_3$ fragment should be described correctly.¹⁶ Accordingly, the first transition shows good agreement between the experimental and calculated energies, which is consistent with its d -character. The second transition shows a discrepancy. Having in mind the extensive π character of the transition, the discussed properties of the CNDO algo-

rithm, however, can serve as an explanation for the difference between the values $36\,000\text{ cm}^{-1}$ (observed) and $42\,700\text{ cm}^{-1}$ (calculated). The experimental and also the calculated spectrum reveals features which are characteristic for charge-transfer transitions. The charge density distribution in the BIT molecule is given on the right-hand side of Table I. The experimental spectrum shows a sharp rise starting at frequencies larger than about $40\,000\text{ cm}^{-1}$ (Fig. 2). So does the calculated spectrum. The transitions at $48\,600$ and $49\,200\text{ cm}^{-1}$ (second one) are examples which show considerable charge transfer between Fe and butadiene (donating) and $(\text{CO})_3$ (accepting). The low charge transfer of most of the transitions indicates the large delocalization of the BIT orbitals and the participation of more than one single-particle transition in a many-particle transition.

IV. RESULTS AND DISCUSSION

Figure 3 shows the remission spectrum $\ln(\kappa/sN)$ versus wave number $\tilde{\nu}$ of BIT adsorbed on BN ($T = 120\text{ K}$). The coverage is $\rho = 1.2$. κ is the absorption and s the scattering coefficient. κ/s has been normalized to the number of adsorbed particles N . Prior to each recorded film spectrum the film had been tempered for $\tau = 7, 18$, or 62 h at about 210 K . After 7 h of tempering time, the film revealed features similar to an untempered film. A film tempered for 62 h , however, revealed stable features which we regard as characteristic of a monolayer or sub-monolayer BIT film. After 18 h an intermediate state was reached. The development of the adsorbed film into the 2D state can be monitored by considering its melting behavior. Figure 4 shows the remission spectrum $\ln(\kappa/sN)$ at $\tilde{\nu} \approx 31\,600\text{ cm}^{-1}$ as a function of temperature, as it developed after the same successive tempering intervals as noted in Fig. 3. One can see that the transition temperature, as it is observed after 7 h (200 K), due to additional tempering (18 h total tempering time), is reduced to about 170 K . However, a second step at 180 K indicates that, obviously, traces of 3D matter are still present which

TABLE I. Experimental (Refs. 14 and 15) and calculated absorption spectrum of the free BIT molecule.

Excitation energies		Oscillator strengths f	Extinction coefficient ϵ_0 (liter mol ⁻¹ cm ⁻¹)	Change of the charge densities at the different ligands		
$\tilde{\nu}_{\text{expt}}^0$ (cm ⁻¹)	$\tilde{\nu}_{\text{calc}}^0$ (cm ⁻¹)			Fe ^a	(CO) ₃ ^a	butadiene ^a
28 000			120			
36 000			2 500			
49 000			13 500			
	29 200 ^b	4.4×10^{-3}		0.057	0.035	-0.092
	42 700	1.0×10^{-1}		-0.001	-0.031	0.031
	43 500	4.9×10^{-4}		-0.025	0.011	0.013
	48 600	1.1×10^{-2}		-0.380	0.519	-0.140
	48 900	5.0×10^{-4}		-0.084	0.059	0.024
	49 200	1.7×10^{-2}		-0.068	0	0.068
	49 200	6.6×10^{-3}		-0.359	0.528	-0.170
	51 500	3.1×10^{-2}		-0.204	-0.032	0.235
	52 600	3.8×10^{-2}		-0.076	0.333	-0.258

^aIn units of one electron charge.

^bCalculated values rounded to $\pm 100\text{ cm}^{-1}$.

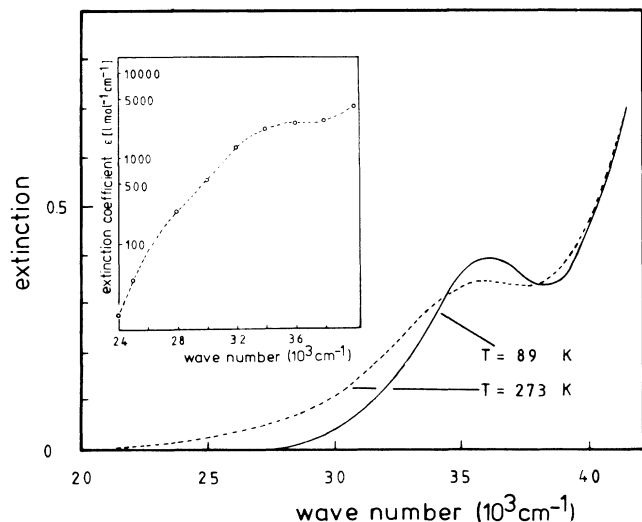


FIG. 2. Absorption spectrum of the free (nonadsorbed) BIT molecule. Extinction E (inset: extinction coefficient ϵ) as a function of wave number $\tilde{\nu}$ at temperatures $T=89$ and 273 K (inset: about $T=295$ K). (After Refs. 14 and 15.)

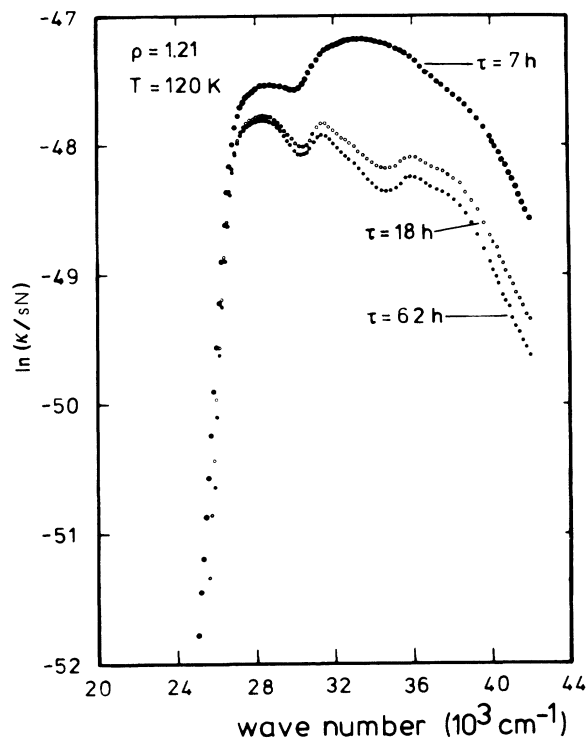


FIG. 3. Remission spectrum $\ln(\kappa/sN)$ versus wave number $\tilde{\nu}$ of BIT adsorbed on BN ($T=120$ K). The coverage is $\rho=1.2$. κ is the absorption and s the scattering coefficient. κ/s has been normalized to the number of adsorbed particles N . Prior to each recorded film spectrum the film had been tempered for $\tau=7, 18$, or 62 h at about 210 K. After 7 h temper time the film revealed similar features as an untempered film. A film tempered for 62 h, however, revealed stable features which we regard as characteristic for a monolayer or submonolayer BIT film.

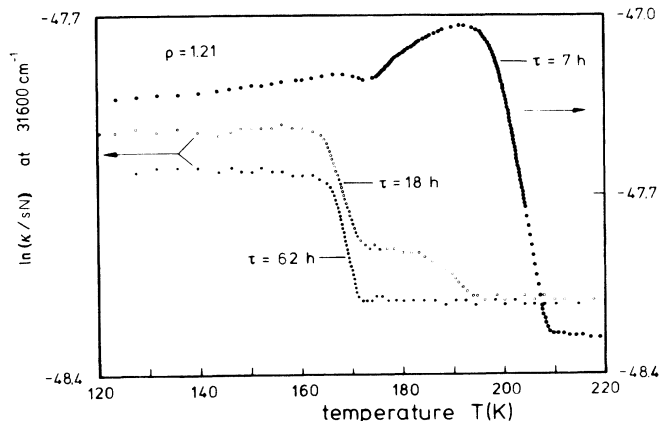


FIG. 4. Remission spectrum $\ln(\kappa/sN)$ at $\tilde{\nu} \approx 31\,600\text{ cm}^{-1}$ as a function of temperature as it has been developed after successive temper intervals, as noted in Fig. 3. The transition temperature as observed after 7 h (200 K) due to additional tempering (18 h total temper time) is reduced to about 170 K. However, a second step at 180 K indicates that, obviously, traces of $3D$ matter are still present which do not melt until now. After 62 h a unique melting transition is observed, indicating a stationary $2D$ state.

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In the stable state the spectrum shows three distinct bands at about $28\,600$, $31\,600$, and $36\,000\text{ cm}^{-1}$. The asymmetry of the $31\,600\text{ cm}^{-1}$ band suggests that under its structured feature two or even three bands may be hidden.

Next, we interpret the experimental observations on the basis of interactions between substrate and BIT adsorbate which lead to conclusions about the possible orientations of an adsorbed BIT molecule on the substrate surface. For these considerations we assume that the BIT adsorbate and BN are in direct contact and that there are no layers consisting of impurities, e.g., in between. To model the interactions between BIT and the BN substrate, we first discuss the orientations which a BIT molecule may assume preferentially. One can think of the BIT molecule as being oriented towards the BN substrate, either with its three CO ligands (BIT-I) or with its butadiene ligand (BIT-II). Both possibilities are shown in Fig. 5.

In the case of BIT-I the 4σ orbitals of CO would interact with π -electron orbitals of BN oriented normally to the surface. Since these orbitals are directed along the C-O axes, overlap with the π system of BN would occur at a disadvantageous angle. Note that only the nitrogen atoms contribute electrons to the π system of BN. Because of its greater electronegativity the nitrogen atom accumulates more negative charge while the boron atom locally carries positive charge. Consequently, the density of π electrons should be lower at the position of the boron atom than at the position of the nitrogen atom. Bonding between the CO ligands and the substrate due to overlap takes place preferentially with partly filled but not between filled orbitals. Therefore, it is advantageous for the CO ligands to

be localized near the boron atoms. In summary, the BIT-I should be positioned at the substrate as depicted in Fig. 5(a). The molecule thereby occupies three BN hexagons.

The second possibility is that the BIT-II molecule rests with its butadiene ligand on the substrate: now the π systems of butadiene and of BN are oriented along a common axis (namely, the normal of the surface), providing optimum overlap. This leads to essentially improved bonding as compared with the analogous BIT-I configuration. In addition, bonding of BIT-II to the substrate is certainly enhanced by the nearly equal bond distances between the C atoms of butadiene [1.45 Å (Refs. 15 and 17)] and that between the B and N atom of BN [1.44 Å (Ref. 18)]. This orientation is depicted in Fig. 5(b).

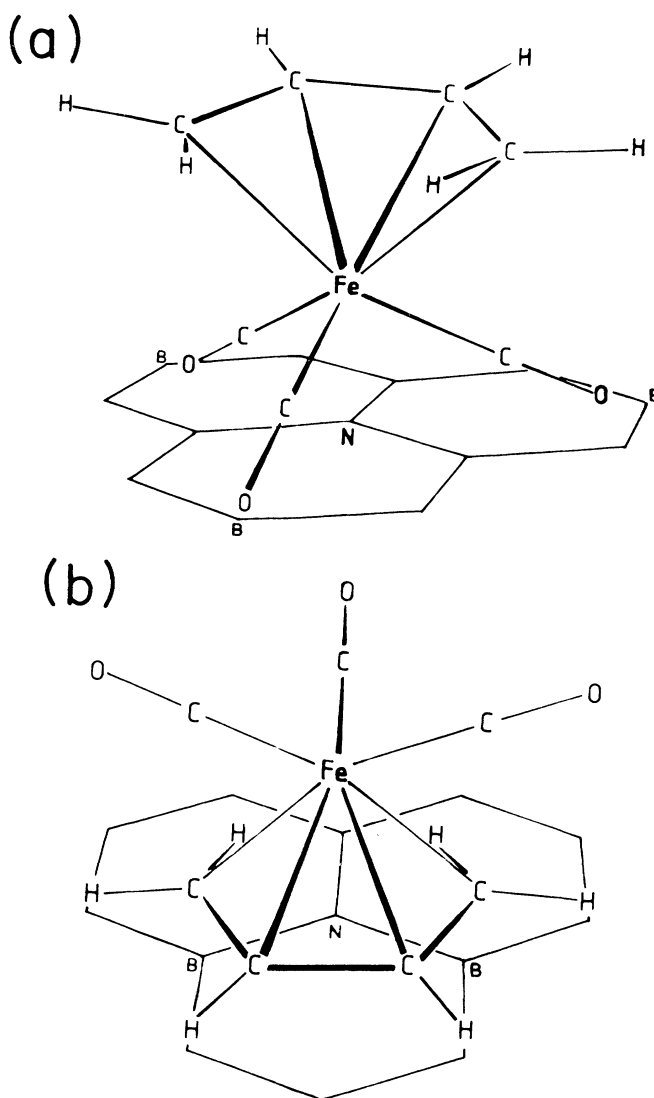


FIG. 5. (a) Assumed BIT-I configuration on BN substrate. The BIT molecule is oriented with its CO ligands towards the surface plane of the substrate. (b) Assumed BIT-II configuration on BN substrate. The BIT molecule is oriented with its butadiene ligand towards the surface plane of the substrate.

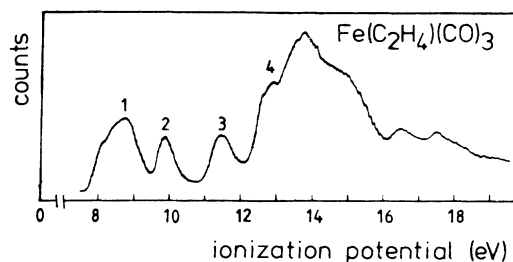


FIG. 6. He-I photoelectron spectrum of the free BIT molecule. Counts as a function of ionization potential. Maxima 1 and 2 correspond to the energy of orbitals having Fe character, maxima 3 and 4 to orbitals of butadiene character. Ion states with CO character are shown between 13.5 and 16 eV. (Ref. 20.)

Other possible configurations corresponding to mixed arrangements (i.e., CO and butadiene ligands are simultaneously in contact with the substrate) are less probable if we consider overlap with the substrate. Overlap between CO and BN and the π systems of butadiene and BN would occur under a very unfavorable condition, since the orbitals are almost perpendicular to each other.

We have carried out calculations of the absorption spectrum of the BIT molecule in either case of orientation. The distance between the substrate and the oxygen atoms of the CO molecules or the carbon atoms of butadiene, respectively, was assumed to be 2.40 Å. Unfortunately, there is no experimental information about the distance between molecule and substrate. 2.40 Å seems plausible for the physisorbed case, since a typical distance in case of chemisorption would be $d=1.80$ Å, as has been observed for CO on a metal substrate, e.g., Ref. 19.

Our calculations are based on "molecules," as shown in Figs. 5(a) and 5(b). The resulting spectra are shown in Tables II and III. The spectra of free BIT (Table I) and those of BIT-I (Table II) are very similar. Table II shows that as compared with free BIT the BIT-I molecule has no additional transitions. The figures listed in the last column of Table II may confirm that there is only weak interaction with the substrate since charge transfer is of order 10^{-3} which increases to 10^{-2} if charge transfer to $(\text{CO})_3$ is involved. This result is in agreement with the arguments given above.

The spectrum of BIT-II, however, contrasts in many aspects with that of free BIT (Table III). The lowest excitation lies at about $24\,600\text{ cm}^{-1}$ and has a fairly large oscillator strength f . Beyond that, additional absorption lines appear between $33\,000$ and $36\,000\text{ cm}^{-1}$ with even higher values of f . These are not present in the case of free BIT and BIT-I. Further transitions between $42\,000$ and $46\,000\text{ cm}^{-1}$ follow. Charge transfer to CO sets in beyond $50\,000\text{ cm}^{-1}$. The substrate contribution to charge transfer lies roughly between 10^{-2} and 10^{-1} electrons and is therefore considerably stronger than in the case of BIT-I, indicating fairly intense interaction with BN. The single-particle states involved in transitions at frequencies below $\tilde{\nu}\approx 50\,000\text{ cm}^{-1}$ originate from molecular orbitals with large d and p character of iron orbitals as well as butadiene orbitals. Molecular orbitals with large CO contri-

TABLE II. Calculated absorption spectrum of the BIT-I molecule.

Excitation energies $\tilde{\nu}^0$ (cm^{-1})	Oscillator strengths f	Change of the charge densities at the different ligands			
		Fe	(CO) ₃ ^a	butadiene ^a	BN ^a
28 500 ^b	6.9×10^{-3}	0.085	-0.008	-0.078	-0.005
42 600	8.3×10^{-4}	-0.012	-0.011	0.028	-0.005
43 800	1.4×10^{-1}	-0.051	-0.107	0.158	-0.001
47 300	1.1×10^{-2}	-0.376	0.547	-0.191	0.021
47 500	9.4×10^{-4}	-0.080	0.029	0.051	0.001
48 100	4.8×10^{-3}	-0.364	0.587	-0.224	0.002
48 900	4.5×10^{-2}	-0.051	-0.020	0.073	0.002
52 300	1.0×10^{-2}	-0.269	0.501	-0.249	0.016
52 800	3.7×10^{-2}	-0.245	0.504	-0.289	0.030

^aIn units of one electron charge.^bValues rounded to $\pm 100 \text{ cm}^{-1}$.

butions are involved in transitions above $\tilde{\nu} \approx 50\,000 \text{ cm}^{-1}$. To compare the experimental with the calculated spectrum it is useful to distinguish three groups: firstly, $24\,000 \text{ cm}^{-1} < \tilde{\nu} < 30\,500 \text{ cm}^{-1}$; secondly (comprehending three new excitations which are characteristic of BIT-II), $33\,000 \text{ cm}^{-1} < \tilde{\nu} < 36\,000 \text{ cm}^{-1}$; finally, $42\,000 \text{ cm}^{-1} < \tilde{\nu} < 46\,000 \text{ cm}^{-1}$. Apart from a systematic shift in frequencies due to the calculational problems, each of the groups is also found experimentally in Fig. 3. The first group can be attributed to the $28\,600 \text{ cm}^{-1}$ transition, the second group to the $31\,600 \text{ cm}^{-1}$ transition, and the third group to the $36\,000 \text{ cm}^{-1}$ transition. The asymmetries appearing in the experimental bands could be attributed to the manifold of bands belonging to each group. As already mentioned, the CNDO algorithm does not correctly predict the positions of the π orbitals. The energy separation between antibonding and bonding orbitals will be overestimated. Because of the correspondence between both the remission and the calculated spectrum we conclude that BIT in its adsorbed state on BN assumes the BIT-II configuration; that means the BIT molecule rests with the butadiene ligand on the BN surface.

As further support for our argumentation we point out that the ionization energies of the π system of the butadiene molecule as revealed by photoemission [Fig. 6 (Ref. 20)] are at the maximum of density of states of BN shown for example in the ESCA spectrum (ESCA is electron spectroscopy for chemical analysis) [Fig. 7 (Ref. 21)]. The lowest ionization energies of CO, on the other hand, are located where BN has a minimum in its density of states. Having in mind that a large density of states at suitable energies strongly promotes bonding, we have one further argument for the configuration of BIT-II.

V. CONCLUSION

In a previous paper¹⁰ we showed that optical remission spectroscopy is suitable to detect phase transitions in physisorbed films and to study their properties in detail, provided that these films consist of molecules which have optical transitions in the visible or near-uv spectral range. In the present paper we demonstrate that remission spectroscopy also proves a surface-sensitive method to determine the orientation of molecules on a surface. This is

TABLE III. Calculated absorption spectrum of the BIT-II molecule.

Excitation energies $\tilde{\nu}^0$ (cm^{-1})	Oscillator strengths f	Change of the charge densities at the different ligands			
		Fe ^a	(CO) ₃ ^a	butadiene ^a	BN ^a
24 600	3.6×10^{-2}	-0.069	-0.065	0.164	-0.033
30 200	7.5×10^{-3}	0.072	-0.006	-0.018	-0.057
33 900	2.6×10^{-2}	0.047	-0.027	0.006	-0.027
34 900	7.1×10^{-3}	0	-0.020	0.042	-0.024
35 200	5.9×10^{-3}	-0.018	-0.059	0.110	-0.033
42 200	1.8×10^{-2}	-0.019	-0.059	0.111	-0.034
42 400	2.2×10^{-2}	-0.110	-0.017	0.112	0.013
42 900	3.5×10^{-2}	-0.007	-0.036	0.082	-0.040
45 300	1.2×10^{-2}	0.064	0.023	-0.053	-0.035
50 400	8.0×10^{-4}	-0.034	-0.060	0.148	-0.056

^aIn units of one electron charge.^bValues rounded to $\pm 100 \text{ cm}^{-1}$.

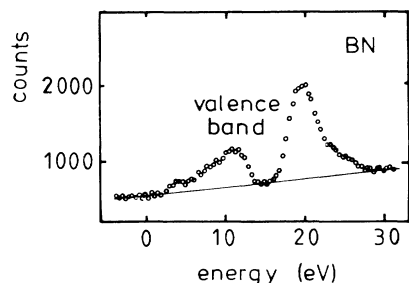


FIG. 7. ESCA spectrum of BN. Counts as a function of energy. The spectrum approximately represents the density of states of BN. (Ref. 21.)

demonstrated for the special example of a BIT molecule. By comparison of the numerically calculated spectrum with that determined experimentally, we are able to show that the molecule should be oriented with its butadiene ligand pointing towards the substrate surface.

The present investigation allows us to foresee possible applications in other fields of surface science. Optical re-mission spectroscopy is besides ellipsometry²² a powerful surface adsorption optical technique and may be applicable to catalytic research and other research on powdered substrates where a simple surface-sensitive spectroscopic technique is of interest.

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¹J. M. Kosterlitz and D. J. Thouless, *J. Phys. C* **6**, 1181 (1973); A. P. Young, *Phys. Rev. B* **19**, 1855 (1979); D. R. Nelson and B. I. Halperin, *ibid.* **19**, 2457 (1979).

²G. Ertl and J. Küppers, *Low Energy Electrons and Surface Chemistry* (Verlag Chemie, Weinheim, 1985), and references therein.

³R. K. Thomas, *Prog. Solid State Chem.* **14**, 1 (1982).

⁴P. A. Heiney, P. W. Stephens, S. G. J. Mochrie, J. Akimitsu, and R. J. Birgeneau, *Surf. Sci.* **125**, 539 (1983).

⁵H. Shechter, J. Suzanne, and J. G. Dash, *Phys. Rev. Lett.* **37**, 706 (1976); H. Shechter, *J. Phys. (Paris) Colloq.* **38**, C4-38 (1977).

⁶R. Marx, *Phys. Rep.* **125**, 1 (1985).

⁷A. Thomy, X. Duval, and J. Regnier, *Surf. Sci. Rep.* **1**, 1 (1981).

⁸B. Vennemann, Ph.D. thesis, University Duisburg, 1984.

⁹G. Kortüm, *Reflexionsspektroskopie* (Springer-Verlag, Berlin, 1969).

¹⁰R. Marx, B. Vennemann, and E. Uffelman, *Phys. Rev. B* **29**,

5063 (1984).

¹¹J. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).

¹²T. A. Albright and R. Hoffmann, *Chem. Ber.* **111**, 1591 (1978).

¹³M. Elian and R. Hoffmann, *Inorg. Chem.* **14**, 1058 (1975); M. Elian, M. L. Chen, D. M. Mingos, and R. Hoffmann, *Inorg. Chem.* **15**, 1148 (1976).

¹⁴O. Jänicke, thesis, University Wien, 1973.

¹⁵H. Weigel, diploma work, University Dortmund, 1976.

¹⁶B. Dick, H.-J. Freund, and G. Hohlneicher, *Mol. Phys.* **45**, 427 (1982).

¹⁷O. S. Mills and C. Robinson, *Acta Crystallogr.* **16**, 758 (1963).

¹⁸*Electrons and Phonons in Layered Crystal Structures*, edited by T. J. Wieting and Schlüter (Reidel, Dordrecht, The Netherlands, 1979).

¹⁹F. Greuter, D. Heskett, E. W. Plummer, and H.-J. Freund, *Phys. Rev. B* **27**, 7117 (1983).

²⁰J. A. Connor, I. M. R. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Molec. Phys.* **28**, 1193 (1974).

²¹H. Hamrin, G. Johansson, U. Gelius, C. Nordling, and K. Siegbahn, *Phys. Scr.* **1**, 277 (1970).

²²M. Dria and G. B. Hess, *Phys. Rev. B* **33**, 4758 (1986).