The chemisorption of methylhydrazine on Pd/Al_2O_3: evidence for the preparation of surface bound alkyldiazenato (CH_3-NN^+) fragments

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Abstract

Qualitative transmission infrared evidence is presented to show that the adsorption of methylhydrazine $(H_3C-NH-NH_2)$ on Pd/Al_2O_3 at 325 K leads to the formation of a methyldiazenato (H_3C-NN^+) surface fragment. Although methylhydrazine contains only single bonds, its adsorption at 325 K leads to the appearance of a vibrational peak near 1950 cm^{-1} where peaks for triple bonds are uniquely found. This proposed structural change is consistent with organometallic chemistry literature reports that describe the products of similar alkylhydrazine reactions with metal complexes as alkyldiazenato ligands. Literature reports of similar surface reactivity exclude alternate interpretations. This result illustrates how interesting stoichiometric processes on surfaces can be identified through the study of precedents within the organometallic chemistry literature. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Methylhydrazine; Methyldiazenato; Infrared spectroscopy; Surface chemical reaction; Palladium

1. Introduction

With increasing interest in the preparation and study of self-assembled monolayers (SAMs) [1–6] on surfaces, there is a concomitant need for strong, thermally stable molecular junctions between the metal surface and monolayer [5,6]. However, the identification of functional groups that can be used as junctions, beyond the standard thiol, organosilane and carboxylate linkages [4], as well as the design of junctions with improved physical properties such as thermal durability, has generated rather little interest [4].

One exception is the isonitrile (**I**) linkage [7,8] that chemisorbs to transition metal surfaces through a bonding mode much like that of CO [9–19]. Its perceived benefit lies with the methyl group attached to the nitrogen atom of the CN moiety, in place of the lone pair [20], to which a wide variety of molecular structures can be attached. Chemisorption through a CN group that is connected to a hydrocarbon chain of conjugated π bonds could ultimately lead to an electro-conductive connection to the surface that may

improve routes to the preparation of microwire arrays [21] and other molecular electronics [22–26].

$$
\begin{array}{c}
CH_3 \\
| \\
N \\
||| \\
C \\
| \\
M
\end{array}
$$

(I)

One similar, though unexplored, candidate junction is manifest by the alkyldiazenato ligand (**II**) [27–29] (R = alkyl) that connects to the metal atom of a complex through a di-nitrogen group instead of the cyanide group but also has an attached alkyl group. It has been extensively studied within organometallic chemistry [27–29] and is distinguished from most coordinated ligands in that it holds a plus one formal charge that has as yet unknown, possibly interesting, surface adsorption properties [27–29] that may include unusual thermal durability [30,31].

$$
\begin{array}{c}
R \\
| \\
N \\
||| \\
N \oplus \\
| \\
M
\end{array}
$$

(II)

The one plus charge that makes alkyldiazenato an interesting surface adsorbate, however, makes it difficult to study since its precursor, usually the benzenediazonium cation (**III**), is prepared and utilized only in cold water, and must be stored over dry ice as the tetrafluoroborate salt [32,33]. While available for the study of SAMs through Langmuir–Blodgett preparation techniques [3], it offers none of the volatility required for careful characterization of its chemisorption bond by UHV surface analysis methods.

(III)
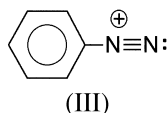
These limitations, however, offer an opportunity to expand upon the so-called ''cluster-surface anal-
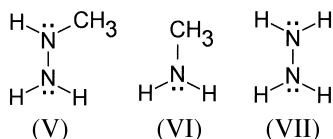
ogy'' [34–36] by looking to stoichiometric synthetic methods within organometallic chemistry to identify a satisfactory preparative route to the surface alkyldiazenato linkage. Indeed, perusal of the organometallic chemistry literature reveals that, instead of the benzenediazonium cation (**III**), a few papers report the use of the organic reactant phenylhydrazine (**IV**) [37–40] to prepare the phenyldiazenato ligand. Exhaustive, exclusive scission of the N−H bonds of the hydrazine group apparently leads to the coordinated ligand. Since these organic precursor molecules are volatile, they offer the opportunity for adsorption onto clean surfaces in a vacuum and characterization by surface sensitive spectroscopies to determine if a similar reaction will occur on a surface. This paper reports vibrational evidence for just such an adsorption of the simpler methylhydrazine molecule (**V**) on the Pd/Al_2O_3 surface.

(IV)
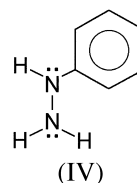
2. Experimental

All spectra were collected using a purged Perkin-Elmer infrared spectrophotometer model #PE-783. A slit program yielding a resolution of 5.4 cm^{-1} was employed and computer assisted data acquisition allowed the use of signal averaging to improve the data's signal-to-noise ratio as well as the subtraction of spectral contributions from the alumina support. The Pd/Al_2O_3 and Al_2O_3 substrates were held on a single CaF_2 disk in the infrared beam in a high vacuum cell having CaF_2 windows whose design has been reported previously [41]. The transmission of the window allowed spectral analyses in the range between 4000 and 1050 cm^{-1}. The cell design allows the sample temperature to lie at any point above 77 K. The preparation of the Pd/Al_2O_3 and Al_2O_3 samples has been reported previously [41]. The trace CO that is found on the fresh Pd surface

was removed according to a previously reported oxygen titration method [19]. Methylhydrazine (**V**) was purchased from Aldrich, degassed in glass ampoules closed by high vacuum stainless steel valves and used without further purification.

$$
\begin{array}{ccc}
\text{H}\diagdown_{\displaystyle \overset{\cdots}{\text{N}}}\diagup^{\text{CH}_3} & \text{CH}_3 & \text{H}\diagdown_{\displaystyle \overset{\cdots}{\text{N}}}\diagup^{\text{H}} \\
\text{H}\diagup^{\displaystyle \overset{\cdots}{\text{N}}}\diagdown_{\text{H}} & \text{H}\diagup^{\displaystyle \overset{|}{\underset{\cdots}{\text{N}}}}\diagdown_{\text{H}} & \text{H}\diagup^{\displaystyle \overset{\cdots}{\text{N}}}\diagdown_{\text{H}} \\
(\text{V}) & (\text{VI}) & (\text{VII})
\end{array}
$$

3. Results

Fig. 1 shows the IR spectra collected between 2200 and 1700 cm^{-1} after the Pd/Al_2O_3 sample was exposed to eight doses of 1×10^{18} molecules of methylhydrazine (**V**) vapor at a surface temperature of 325 K. With increasing exposure, a broad peak near 1950 cm^{-1} grows in along with a shoulder to higher frequency near 2050 cm^{-1}. The position and width of these peaks are inconsistent with those of background CO [42] but similar to those of adsorbed methylisocyanide (**I**) [19]. Data not shown indicates that this peak structure attenuates only slightly with mild heating. No peaks are visible in the $\nu(CH)$
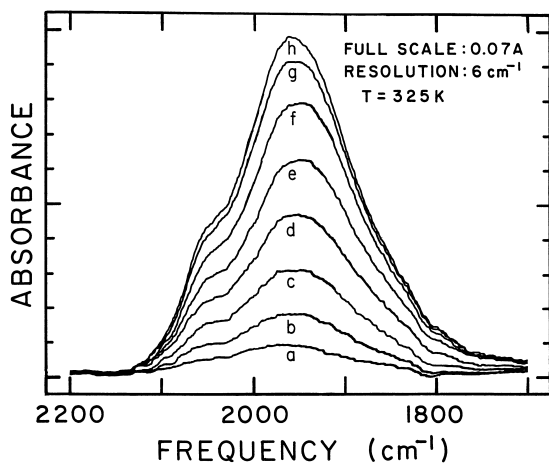
vibrational region and only exceedingly weak peaks (not shown) near 1402 and 1427 cm^{-1} in the $\delta(CH_3)$ methyl deformation region could be detected.

4. Discussion

4.1. Selection of an appropriate surface

Since few reports of alkylhydrazine adsorption have appeared [43–45], a palladium surface can be shown as a wise choice for this study by perusing the extensive surface science literature covering the adsorption and reaction of methylamine (**VI**) [46–52] and hydrazine (**VII**) [53–64]. The C–H, C–N and N–H bonds of methylamine and the N–N and N–H bonds of hydrazine include all the bond types found in methylhydrazine and offer clues to a successful surface reaction by determining which bonds will break first on which surfaces.
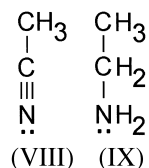
For example, while initial C–N bond scission is favored on Ni(100) [46], it is disfavored on Rh(111) [47], Ni(111) [52] and Pd(111) [48,50]; some C–N bond scission is seen on Ru(001) [51] and Pt(100) [49]. On Pd(111) [50], N–H scission occurs more readily than C–H scission; on Ru(001) [51], the reverse is observed. On Ni(111) [52], the C–H and N–H bond scission occur about equally. On Ni(111) [53], Pd(100) [63], and polycrystalline Fe [62], N–N scission is favored over N–H scission; on Pt(111) [54] and Ir(111) [61], the reverse is seen. On Ru(001) [55], Rh(100) [59], Rh(111) [58] and polycrystalline Rh [57,64], Pt [60] and Pd [56], both occur.

Since a reaction to form alkyldiazenato adsorbates from alkylhydrazines requires exclusive N–H bond scission, these literature results suggest a successful reaction on supported Pd since the Pd(111) surface disfavors C–N bond scission [51] and favors N–H scission over C–H scission [50]. Pd(100) does favor the undesirable N–N scission over N–H scission [63] but (100) planes are less common on supported Pd [65–67].

4.2. Characterization of adsorbed methylhydrazine

Since methylhydrazine (**V**) contains only single bonds in the vapor phase, and since it is well known

Fig. 1. Transmission infrared spectra of methylhydrazine (**V**) chemisorbed on Pd/Al_2O_3 as a function of increasing exposure at 325 K. Cumulative exposures are (a) 1×10^{18}, (b) 2×10^{18}, (c) 3×10^{18}, (d) 4×10^{18}, (e) 5×10^{18}, (f) 6×10^{18}, (g) 7×10^{18}, and (h) 8×10^{18} molecules.

within synthetic chemistry that few bonds beside the triple bond are associated with intense vibrational absorptions near 1950 cm^{-1} [68], it can at the outset be concluded that, upon adsorption at 325 K, methylhydrazine's molecular structure undergoes significant modification that likely includes the creation of a triple bond (Fig. 1). This structural change is consistent with literature reports that describe the formation of alkyldiazenato ligands through the reaction of alkylhydrazines with metal complexes [37–39,69] and is similar to a report describing the desorption of weakly adsorbing acetonitrile (**VIII**) following the adsorption of saturated ethylamine (**IX**) on oxygen pre-covered Ag(110) [70]. The formation of a triply bonded adsorbate from a saturated precursor is more generally precedented by the well known surface ''decomposition'' of the saturated methanol molecule [71–73] to form adsorbed, triply bonded CO through a likewise exhaustive scission of O−H and C−H bonds.

$$
\begin{array}{cc}
\mathrm{CH_3} & \mathrm{CH_3} \\
| & | \\
\mathrm{C} & \mathrm{CH_2} \\
||| & | \\
\mathrm{N} & \mathrm{NH_2} \\
\ddot{} & \ddot{} \\
\mathrm{(VIII)} & \mathrm{(IX)}
\end{array}
$$

Previously reported adsorption studies on Pd surfaces tend to exclude outcomes other than that of the formation of a surface alkyldiazenato fragment. C−N bond scission to produce a surface di-nitrogen adsorbate to account for the peak at 1950 cm^{-1} can be excluded since the reaction is disfavored on Pd(111) [48,50] and since di-nitrogen has been reported to desorb from Pd at temperatures well below that of the surface temperature (325 K) [74,75]. For N−N bond scission to form adsorbed CN^{-} is also unlikely even though N−N scission is favored on the less common Pd(100) surface [63] and CN-adsorbed on Pd(111) has vibrational peaks with energies similar to those shown in Fig. 1 [76]. Surface hydrogen has been reported to hydrogenate adsorbed CN^{-} on Pd at temperatures below 325 K [77] and lead to adsorbed HCN showing vibrational peaks with energies lower than those shown in Fig. 1 [77]. Since CN formation would require the release of at least the methyl group hydrogen atoms to the surface, this reaction would not seem to be the reaction taking place in this study.

Alkyldiazenato ligands in complexes display a broad range of ν(NN) vibrational energies that fall between 1950 and 1450 cm^{-1} [31,78–81]. This range is due to a variety of coordination modes [29] that arise when one or both alkyldiazenato nitrogen atoms rehybridize from the sp, found in the benzenediazonium cation (**III**) [29], to sp^2. This has led to a not unusual experimental dependence on X-ray crystallography to characterize complexes containing these ligands [37–39,69,79,81]. Conjugation with the benzene ring also affects the vibrational energy [82].

However, since the energy of the peak in Fig. 1 lies on the high end of the range of characterized vibrational modes, its assignment is simplified and can be attributed to the linear alkyldiazenato ligand that has appeared in at least one complex [31] and displays a vibrational frequency similar to that of the peaks shown in Fig. 1. The vibrational frequency is also similar to that of an isoelectronic, linear, threefold bridging methylisocyanide (**I**) ligand reported on a nickel cluster [83], which may indicate a threefold bridging alkyldiazenato surface fragment (Fig. 2B). The assignment of the high frequency shoulder at 2050 cm^{-1} (Fig. 1) could then indicate adsorption to a two-fold bridging site (Fig. 2A). This assignment would be consistent with a similar methylisocyanide adsorbate mode reported on Pd/Al$_2$O$_3$ [19] but should be considered cursory at this point.

The similarity of the data in Fig. 1 with that of adsorbed methylisocyanide [19] also involves the unusual peak widths found in both sets of data relative to that of adsorbed CO [42]. While a complete peak width analysis is beyond the scope of this report, the similarity might suggest an inverse association of peak width with triple bond dipole moment.

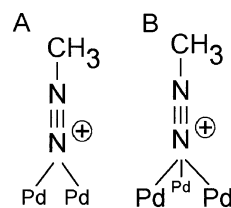The absence of ν(C−H) peaks in the IR data need not be a contra-indication of surface methyl-

$$
\begin{array}{cc}
\mathrm{A} & \mathrm{B} \\
\mathrm{CH_3} & \mathrm{CH_3} \\
| & | \\
\mathrm{N} & \mathrm{N} \\
||| \oplus & ||| \oplus \\
\mathrm{N} & \mathrm{N} \\
\diagup \diagdown & \diagup | \diagdown \\
\mathrm{Pd} \quad \mathrm{Pd} & \mathrm{Pd}^{\,\mathrm{Pd}}\, \mathrm{Pd}
\end{array}
$$

Fig. 2. Possible structures of surface fragments resulting from the adsorption of methylhydrazine on Pd/Al$_2$O$_3$ at 325 K. (A) two-fold bridging methyldiazenato and (B) three-fold bridging methyldiazenato.

diazenato. The ν(C−H) peaks have already, without explanation, been reported absent for the methyl group of surface ethylidyne on Pd/Al$_2$O$_3$ [84] while being detectable on Pt, Rh and Ru [84]. The same effect operating for surface ethylidyne could, therefore, be operating for adsorbed methyldiazenato as well. Of course, while the absence of a peak is not a positive indicator of a structure, the arguments already presented seem to satisfactorily eliminate all other likely possibilities.

High intensity δ(CH$_3$) peaks, unlike this study, are seen for ethylidyne adsorbed on Pd/Al$_2$O$_3$ [84]. However, their low intensity in this study could be due to the same effect reported for isotopically labeled ethylidyne on Ni(111) [85] where the additional mass of the deuterium fostered a mixing of the δ_s(CD$_3$) mode with the ν(C−C) mode leading to a loss of dipole activity for the δ_s(CD$_3$) mode. In this study the additional mass may arise from the additional nitrogen atom of the methyldiazenato structure.

The assignment of the peak in Fig. 1 to an alkyldiazenato adsorbate is also strengthened because a similar hydrodiazenato (H−NN +) adsorbate has quite possibly been detected, but not described, in an HREELS study of hydrazine (**VII**) chemisorption on Ru(001) [55]. In this work, a peak near 2000 cm^{-1} appears after thermal processing of an adsorbed hydrazine overlayer to above 300 K [55, Fig. 8]. It is attributed to adsorbed background CO although: (1) no measurements were reported of background CO adsorption on the clean surface, (2) the base pressure in the chamber was 5×10^{-11} mbar and (3) the surface was saturated with hydrazine prior to thermal processing [55].

The assignment of this peak to background CO can be called into question because the adsorption of deuterated hydrazine [55, Fig. 9] did not lead to a duplicate impurity peak at 2000 cm^{-1}. However, a peak 35 cm^{-1} to lower energy was detected in the deuteration study and it behaved much like the 2000 cm^{-1} peak in the initial hydrazine study [55, Fig. 8]. This suggests that both peaks could be associated with a hydrazine decomposition product containing at least one hydrogen or deuterium atom. If the decomposition product is assumed to be hydrodiazenato (**II**) (R = H), rough calculation (given the broadness and low intensity of the loss peaks) of an

isotope shift [86] for the presumed ν(NN−H/D) stretch leads to a frequency shift similar to the 35 cm^{-1} value seen between the above two described peaks. While the 2000 cm^{-1} peak was assigned based on direct studies of CO adsorbed on Ru(001) [87], assignment to a hydrodiazenato adsorbate seems to be an equally distinct possibility.

While this initial study does not have the quantitative rigor of a customary surface analysis study, it makes thorough use of the ''exclusionary'' arguments of qualitative molecular analysis [86] common among synthetic chemists and therefore available for application to surface systems. While nitrogen isotopic labeling studies and single crystal characterization methods like LEED analysis will allow a more definitive assignment of the reported vibrational peaks, and while further studies will be needed to understand the scope of alkylhydrazine surface reactivity, the above results indicate that the hydrazine functional group is a likely precursor to the surface alkyldiazenato linkage on Pd.

The prospect of enhanced thermal durability of this alkyldiazenato junction [30,31] makes it of particular interest in the study of SAMs. Its additional thermal durability can be rationalized to arise from both the one plus charge of the uncoordinated R−NN + fragment [27–29] and its likely normal orientation as a linear surface adsorbate. The one plus charge of the uncoordinated fragment will lead to a high energy desorption product that will disfavor desorption thermodynamically. The suggested normal lying linear adsorbate structure does not seem able to provide a low energy vibrational mode that can bring the outer adsorbate atoms close enough to the surface so that decomposition could progress through any other low energy pathway.

This work also reveals a new opportunity to expand upon the ''cluster-surface'' analogy [34–36] between metal complexes and surfaces through the application of insight gained from stoichiometric organometallic chemistry reactions to the preparation of surface adsorbate fragments.

5. Conclusion

Transmission infrared data suggests that methylhydrazine adsorbed on Pd/Al$_2$O$_3$, in analogy with

published organometallic chemistry reports, reacts to form, through exhaustive N–H bond scission, a methyldiazenato surface fragment that contains a bound di-nitrogen moiety with an attached methyl group. This is indicated by: (1) the appearance of a vibrational peak near 1950 cm^{-1} even though the precursor adsorbate contains only single bonds with lower vibrational energies and (2) comparison of the data with that of reported surface reactions that excludes other possibilities. These results indicate that (A) further study of adsorbed alkylhydrazines is warranted, (B) the hydrazine precursor offers promise for a new, possibly thermally durable, linking group for the study of SAMs, and (C) insight into possible stoichiometric surface reactions can be gained by careful study of the organometallic chemistry literature.

Acknowledgements

References

[1] G.M. Whitesides, Sci. Am. 273 (1995) 146.
[2] G.K. Jennings, P.E. Laibinis, J. Am. Chem. Soc. 119 (1997) 5208.
[3] L.H. Dubois, R.G. Nuzzo, Annu. Rev. Phys. Chem. 43 (1992) 437.
[4] A. Ullman, Chem. Rev. 96 (1996) 1533.
[5] J.D. Swalen, D.L. Allara, J.D. Andrade, E.A. Chandross, S. Garoff, J. Israelachvili, T.J. McCarthy, R. Murray, R.F. Pease, J.F. Rabolt, K.J. Wynne, H. Yu, Langmuir 3 (1987) 932.
[6] Y. Xia, G.M. Whitesides, Angew. Chem. Int. Ed. 37 (1998) 550.
[7] J.J. Hickman, C. Zou, D. Ofer, P.D. Harvey, M.S. Wrighton, J. Am. Chem. Soc. 111 (1989) 7271.
[8] J.M. Seminario, A.G. Zacarias, J.M. Tour, J. Am. Chem. Soc. 121 (1999) 411.
[9] R.R. Cavanaugh, J.T. Yates Jr., J. Chem. Phys. 75 (1981) 1551.
[10] S. Semancik, G.L. Haller, J.T. Yates Jr., J. Chem. Phys. 78 (1983) 6970.
[11] T. Szilagyi, Appl. Surf. Sci. 35 (1988) 19.
[12] A.C. Ontko, R.J. Angelici, Langmuir 14 (1998) 1684.
[13] C.M. Friend, E.L. Muetterties, G.L. Gland, J. Phys. Chem. 85 (1981) 3256.
[14] N.R. Avery, T.W. Matheson, B.A. Sexton, Appl. Surf. Sci. 22–23 (1985) 384.
[15] S.T. Ceyer, J.T. Yates Jr., J. Phys. Chem. 89 (1985) 3842.
[16] N.R. Avery, T.W. Matheson, Surf. Sci. 143 (1984) 110.
[17] C.M. Friend, J. Stein, E.L. Muetterties, J. Am. Chem. Soc. 103 (1981) 767.
[18] W.P. Griffith, Coord. Chem. Rev. 17 (1975) 177.
[19] M.R. Albert, J. Catal. 189 (2000) 158.
[20] R. Hofffmann, M.M.-L. Chen, D.L. Thorn, Inorg. Chem. 16 (1977) 503.
[21] L.A. Bumm, J.J. Arnold, M.T. Cygan, T.D. Dunbar, T.P. Burgin, L. Jones II, D.L. Allara, J.M. Tour, P.S. Weiss, Science 271 (1996) 1705.
[22] C.A. Mirkin, M.A. Ratner, Annu. Rev. Phys. Chem. 43 (1992) 719.
[23] A. Aviram, M. Ratner (Eds.), Molecular Electronics, Science and Technology, Annals of the New York Academy of Sciences 852 New York Academy of Sciences, New York, 1998, p. 197.
[24] J.M. Tour, M. Kozaki, J.M. Seminario, J. Am. Chem. Soc. 120 (1998) 8486.
[25] Y. Wada, Surf. Sci. 386 (1997) 265.
[26] C.P. Collier, E.W. Wong, M. Belohradský, F.M. Raymo, J.F. Stoddart, P.J. Kuekes, R.S. Williams, J.R. Heath, Science 285 (1999) 391.
[27] W.A. Hermann, Adv. Organomet. Chem. 20 (1982) 159.
[28] W.A. Hermann, Angew. Chem. Int. Ed. Engl. 17 (1978) 800.
[29] D. Sutton, Chem. Soc. Rev. 4 (1975) 443.
[30] S. Trofimenko, Inorg. Chem. 8 (1969) 2675.
[31] W.A. Herrmann, J. Organomet. Chem. 84 (1975) C25.
[32] R.B. King, M.B. Bisnette, Inorg. Chem. 5 (1966) 300.
[33] A.I. Vogel, in: Practical Organic Chemistry, Longmans, Green, New York, 1956, p. 609.
[34] E.L. Muetterties, T.N. Rhodin, E. Band, C.F. Brucker, W.R. Pretzer, Chem. Rev. 79 (1979) 91.
[35] M.R. Albert, J.T. Yates Jr., The Surface Scientist's Guide to Organometallic Chemistry, ACS Books, Washington, DC, 1987.
[36] A.M. Bradshaw, Surf. Sci. 331–333 (1995) 978.
[37] V.F. Duckworth, P.G. Douglas, R. Mason, B.L. Shaw, J. Chem. Soc., Chem. Commun. 70 (1970) 1083.
[38] D. Petredis, A. Burke, A.L. Balch, J. Am. Chem. Soc. 92 (1970) 428.
[39] R. Mason, K.M. Thomas, J.A. Zubieta, P.G. Douglas, A.R. Galbraith, B.L. Shaw, J. Am. Chem. Soc. 96 (1974) 260.
[40] M.L.H. Green, T.R. Sanders, R.N. Whitely, Z. Naturforsch. 23b (1968) 106.
[41] J.T. Yates Jr., T.M. Duncan, S.D. Worley, R.W. Vaughn, J. Chem. Phys. 70 (1979) 1219.
[42] P. Gelin, A.R. Seidle, J.T. Yates Jr., J. Phys. Chem 88 (1984) 2978.

[43] J.S. Somers, M.E. Bridge, Surf. Sci. 159 (1985) L439.

[44] A.L. Schwaner, M. Kovar, D.J. Alberas, J.M. White, J. Vac. Sci. Technol. A 13 (1995) 1368.

[45] Y. Bu, D.W. Shinn, M.C. Lin, Surf. Sci. 276 (1992) 184.

[46] C.-C. Chang, C. Khong, R. Saiki, J. Vac. Sci. Technol. A 11 (1993) 2122.

[47] S.Y. Hwang, A.C.F. Kong, L.D. Schmidt, J. Phys. Chem. 93 (1989) 8327.

[48] S.Y. Hwang, E.G. Seebauer, L.D. Schmidt, Surf. Sci 188 (1987) 219.

[49] P.A. Thomas, R.I. Masel, J. Vac. Sci. Technol. A 5 (1987) 1106.

[50] J.J. Chen, N. Winograd, Surf. Sci. 326 (1995) 285.

[51] D.F. Johnson, Y. Wang, J.E. Parmeter, M.M. Hills, W.H. Weinberg, J. Am. Chem. Soc. 114 (1992) 4279.

[52] I. Chorkendorff, J.N. Russell Jr., J.T. Yates Jr., J. Chem. Phys. 86 (1987) 4692.

[53] J.L. Gland, G.B. Fisher, G.E. Mitchell, Chem. Phys. Lett. 119 (1985) 89.

[54] D.J. Alberas, J. Kiss, Z.-M. Liu, J.M. White, Surf. Sci. 278 (1992) 51.

[55] H. Rauscher, K.L. Kostov, D. Menzel, Chem. Phys. 177 (1993) 473.

[56] G. Ertl, J. Tornau, Z. Phys. Chem. NF 93 (1974) 109.

[57] J. Prasad, J.L. Gland, Surf. Sci. 258 (1991) 67.

[58] M.L. Wagner, L.D. Schmidt, Surf. Sci. 257 (1991) 113.

[59] W.M. Daniel, J.M. White, Surf. Sci. 171 (1986) 289.

[60] G.A. Papapolymerou, L.D. Schmidt, Langmuir 3 (1987) 1098.

[61] H.H. Sawin, R.P. Merrill, J. Chem. Phys. 73 (1980) 996.

[62] M.H. Matlook, M.W. Roberts, in: J. Chem. Res. S, 1977, p. 336.

[63] R. Dopheide, L. Schröter, H. Zacharias, Surf. Sci. 257 (1991) 86.

[64] J. Prasad, J.L. Gland, Langmuir 7 (1991) 722.

[65] K. Wolter, O. Seiferth, H. Kuhlenbeck, M. Bäumer, H.-J. Freund, Surf. Sci. 399 (1998) 190.

[66] R.L. Burwell Jr., Langmuir 2 (1986) 2.

[67] R. van Hardeveld, F. Hartog, Surf. Sci. 15 (1969) 189.

[68] G. Herzberg, Molecular Spectra and Molecular Structure: II. Infrared and Raman Spectra of Polyatomic Molecules, D. van Nostrand, New Jersey, 1956.

[69] J.R. Boehm, A.L. Balch, K.F. Bizot, J.H. Enemark, J. Am. Chem. Soc 97 (1975) 501.

[70] D.M. Thornburg, R.J. Madix, Surf. Sci. 226 (1990) 61.

[71] J.N. Russell Jr., S.M. Gates, J.T. Yates Jr., Surf. Sci. 146 (1984) 199.

[72] J.N. Russell Jr., S.M. Gates, J.T. Yates Jr., Surf. Sci. 159 (1984) 233.

[73] J.N. Russell Jr., S.M. Gates, J.T. Yates Jr., Surf. Sci. 163 (1984) 516.

[74] M. Bertolo, K. Jacobi, Surf. Sci 265 (1992) 1.

[75] K. Horn, J.D. Dinardo, W. Eberhardt, H.-J. Freund, E.W. Plummer, Surf. Sci. 118 (1982) 465.

[76] M.E. Kordesh, W. Stenzel, H. Conrad, Surf. Sci. 186 (1987) 601.

[77] M.E. Kordesh, W. Stenzel, H. Conrad, Surf. Sci. 175 (1986) L687.

[78] K.R. Laing, S.D. Robinson, M.F. Uttley, J. Chem. Soc., Dalton Trans. (1973) 2713.

[79] A.P. Gaughan Jr., B.L. Haymore, J.A. Ibers, W.H. Myers, T.E. Nappier Jr., D.W. Meek, J. Am. Chem. Soc. 95 (1973) 6859.

[80] B.L. Haymore, J.A. Ibers, J. Am. Chem. Soc. 95 (1973) 3052.

[81] K.D. Schramm, J.A. Ibers, J. Am. Chem. Soc. 100 (1978) 2932.

[82] G.W. Parshall, J. Am. Chem. Soc. 87 (1965) 2133.

[83] K.S. Ratliff, G.K. Broeker, P.E. Fanwick, C.P. Kubiak, Angew. Chem. Int. Ed. Engl. 29 (1990) 395.

[84] T.P. Beebe Jr., J.T. Yates Jr., J. Phys. Chem. 91 (1987) 254.

[85] T. Bürgi, T.R. Trautman, K.L. Haug, A.L. Utz, S.T. Ceyer, J. Phys. Chem. B 102 (1998) 4952.

[86] D.J. Pasto, C.R. Johnson, Organic Structure Determination, Prentice-Hall, London, 1969.

[87] G.E. Thomas, W.H. Weinberg, J. Chem. Phys. 70 (1979) 1437.