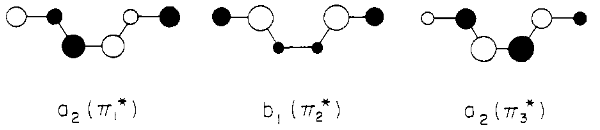
Chart I



Support for the above interpretation is provided by ab initio minimal (STO-3G) and split-valence (3-21G) basis set calculations[9] on *cis*- and *trans*-hexatriene. With the minimal basis set, long-range through-space interactions are not possible, while such interactions are possible with the split-valence basis set. The 3-21G calculations predict, in good agreement with experiment, that the second π^* orbital of the cis isomer is 0.41 eV below that of the trans isomer and that the π orbital energies agree to 0.09 eV. At the STO-3G level the second π^* orbital of the cis isomer is only 0.16 eV more stable than that of the trans. The 3-21G calculations further predict that the first π^* orbital energy is essentially the same for the two isomers and that the third π^* orbital is stabilized by 0.38 eV in the trans isomer. Unfortunately the latter prediction cannot be verified experimentally because of the small size of the π^*_3 structure and its overlap with the π^*_2 feature in the spectrum of the trans isomer.

We note that the importance of the increased diffuseness of anion wave functions has been discussed previously in various contexts.[6,10–12] In particular, we note that calculations by Staley et al.[12] have shown that the C_1–C_4 interaction in the first π^* orbital of *cis*-butadiene increases as the basis set is made more diffuse and that this π^* orbital is expected to be more stable in the cis than in the trans isomer. ETS studies on cyclic dienes[12,13] have provided experimental evidence of the importance of the C_1–C_4 interaction in these compounds. The present measurements, however, show directly that certain electron affinities will be appreciably different in cis and trans isomers. Such effects may be anticipated in the first and third π^* orbitals of 1,3,5,7-octatetraene, for example.

The role of such long-range through-space interactions on particular electronic states in the neutral molecule remains to be assessed. The available experimental data[2] on the excitation energies of *cis*- and *trans*-hexatriene fail to display appreciable differences, and large basis set calculations are available only for the trans isomer. The lowest dipole forbidden transition, in which one might expect to see a difference in the excitation energies of the two isomers, has not yet been observed or, at least, not yet unambiguously assigned.[14]

Finally, since the cis isomer of the *neutral* molecule is expected to be only slightly less stable than the trans, 0.13 eV according to force field calculations,[15] the present results indicate that the second *anion* state of the cis structure will be appreciably more stable, ~0.4 eV, than the trans.

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Registry No. *cis*-1,3,5-Hexatriene, 2612-46-6; *trans*-1,3,5-hexatriene, 821-07-8.

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On the Origins of the Blue Shift of the Carbonyl n–π^* Transition in Hydrogen-Bonding Solvents

Peter R. Taylor

CSIRO Division of Chemical Physics
Clayton, Victoria, Australia 3168

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In hydrogen-bonding solvents the carbonyl n–π^* transition undergoes a blue shift of some 0.13–0.25 eV. Traditionally,[1–3] this shift has been regarded as due to the lowering of the ground-state energy by hydrogen bonding, the excited state supposedly showing little or no hydrogen bonding. (The possible influence of geometry changes was considered by Pimentel,[2] although this aspect seems to have received little attention recently.) Assuming that only the ground-state energy is lowered appreciably by hydrogen bonding, the T_e value of the n–π^* transition would be increased by the hydrogen-bond energy, with which the blue shift is then identified. A number of theoretical calculations appear to support this viewpoint.[4,5]

Recently, however, Beecham and co-workers have advanced a different interpretation of the blue shift in α,β-unsaturated ketones.[6,7] CD spectra, in which the vibrational structure of the n–π^* band was resolved, were obtained; in these spectra the blue shift arises entirely (to within 0.004 eV) from intensity redistribution among vibrational subbands. These observations are incompatible with the traditional viewpoint outlined above: the absence of a shift in T_e implies that the excited state remains hydrogen bonded and a blue shift occurs because the geometries of the ground and excited states of the solute are affected differently by hydrogen bonding. A model calculation was used in ref 7 to predict an extension of the excited state carbonyl CO bond due to hydrogen bonding.

The purpose of the present study is to demonstrate that even in the simplest carbonyl excited state a hydrogen bond is formed, and to advance an explanation for the blue shift based on geometry changes on hydrogen bonding. The system studied is formaldehyde–water. As the molecules studied by Beecham and Hurley[6] remain planar in their excited states, only planar geometries were considered in this work. This also facilitates comparison with the work of Del Bene.[4] Within this restriction, the geometries of $\tilde{X}(^1A_1)H_2CO$, $\tilde{A}(^1A_2)H_2CO$, $\tilde{X}(^1A_1)H_2O$, $\tilde{X}(^1A')H_2CO$–H_2O, and $\tilde{A}(^1A'')H_2CO$–H_2O were fully optimized by using SCF gradient techniques.[8] Labeling of atoms for reference is shown in Figure 1. A double ζ Gaussian basis[9] augmented with one set of polarization functions ($\alpha_d(C) = 0.7$, $\alpha_d(O) = 1.2$, $\alpha_p(H) = 0.8$) was used on each atom. All calculations were performed with the MOLECULE program system[10] as implemented on the CSIRONET Cyber 70/Model 76. Geometry parameters are converged to at least the figures given.

The optimized $\tilde{X}$- and $\tilde{A}$-state geometries of H_2CO–H_2O are given in Table I, together with the optimized values for the free solute and solvent. Hydrogen-bond energies (E_H), computed by using a counterpoise correction for superposition errors,[11] are also given; they show clearly that a strong hydrogen bond exists in the $\tilde{A}(^1A'')$ state. Noteworthy is the large CO_1H_{21} angle of this bond; a very weak hydrogen bond was observed at smaller (120–150°)

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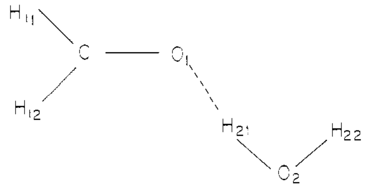

Figure 1. Labeling of atoms in H_2CO-H_2O.

Table I. H_2CO-H_2O and Component Geometries[a]

	$X(^1A')$	$A(^1A'')$
$r(CO_1)$	1.188 (1.184)	1.358 (1.351)
$r(CH_{11})$	1.104 (1.104)	1.079 (1.081)
$r(CH_{12})$	1.104 (1.104)	1.079 (1.081)
$\angle(H_{11}CO_1)$	121.6 (122.1)	116.6 (118.8)
$\angle(H_{11}CH_{12})$	116.6 (115.8)	126.8 (122.4)
$r(O_2H_{21})$	0.958 (0.950)	0.951 (0.950)
$r(O_2H_{22})$	0.951 (0.950)	0.949 (0.950)
$\angle(H_{21}OH_{22})$	102.5 (105.4)	105.9 (105.4)
$r(O_1H_{21})$	1.898	2.143
$\angle(CO_1H_{21})$	116.4	166.6
$\angle(CO_1O_2)$	116.7	165.6
E_H, kcal/mol	2.9	1.9

[a] Component geometries in parentheses. Distances in Å, angles in degrees.

Table II. n–π^* Excitation Energies (eV)

	$\Delta E_{\text{vertical}}$	$\Delta E_{\text{adiabatic}}$ (T_e)
H_2CO	3.42 (3.50)[a]	2.52
H_2CO-H_2O	3.57	2.57

[a] Experiment (ref 13).

angles by Iwata and Morokuma.[5] Unlike the conclusion of Del Bene[4] that there is no excited-state hydrogen bond near the *ground*-state geometry, the variation of energy with $r(O_1H_{21})$ at CO_1H_{21} = 120° is not purely repulsive[4] but gives a weak (~0.5 kcal/mol) bond at larger (~2 Å) r values, as could be inferred from the work of Iwata and Morokuma.[5]

Changes induced in the internal geometry of solute and solvent are generally small (Table I). Exceptions are the closing of the water HOH angle in the $\tilde{X}(^1A')$ state and the very large increase in $H_{11}CH_{12}$ in the $\tilde{A}(^1A'')$ state. Clearly, such changes in the r_e geometries will, as a result of the Franck–Condon principle,[2,12] alter the vibrational band structure of the n–π^* transition relative to the non-hydrogen-bonded case. It may be noted that the prediction of Beecham et al. that $r(CO_1)$ in the excited state is considerably increased on hydrogen bonding is not substantiated in this study.

Vertical and adiabatic (T_e) n–π^* transition energies are given in Table II. While a vertical blue shift is indeed observed, it is evident that little of it arises from a change in T_e. The major component of the blue shift arises from the changes induced in the component molecule geometries by hydrogen bonding. Naturally, studies such as those of ref 4 and 5, in which component geometries are held frozen, may predict a blue shift but cannot provide information on its origins. On the other hand, given that the solute excited state can sustain a strong hydrogen bond and given the "Franck–Condon" origins of the blue shift, it is not justifiable to identify experimentally determined blue shifts with hydrogen-bond energies.[2]

A study of nonplanar geometries, together with a more extensive discussion of the planar results (including basis set comparisons) will be given in a forthcoming publication.

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Registry No. H_2CO, 50-00-0; H_2O, 7732-18-5.

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Effect of Particle Size on the Activity of Supported Palladium Catalysts

Yoshio Takasu,* Tsutomu Akimaru, Kenji Kasahara, and Yoshiharu Matsuda

Faculty of Engineering, Yamaguchi University
Tokiwadai, Ube 755, Japan

Hiroyuki Miura and Isamu Toyoshima

Research Institute for Catalysis
Hokkaido University, Sapporo 060, Japan

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We have performed experiments on the kinetics of the H_2–D_2 exchange reaction in the presence of a Pd/C model catalyst. Our results reveal that the phenomenological activation energy for this reaction increases with a decrease in the average palladium particle size.

Many experiments have been carried out in order to study the effect of particle size in supported metal catalysts prepared by impregnation or precipitation.[1] However, such preparation methods make it difficult to observe fine metal particles, to prepare clean metal surfaces, and to characterize the surface of the catalyst particles by electron spectroscopy. These difficulties may be substantially overcome by using a model catalyst, consisting of metal particles evaporated onto a carbon film within an ultra-high-vacuum system.[2-8] For example, Doering and co-workers[7,8] were able to examine the effect of particle size on the chemisorption and desorption kinetics of carbon monoxide by Pd/mica and Ni/mica model catalysts. These workers found a dramatic decrease in the rate of carbon formation, as the average particle size decreased.

In the present study we investigated the effect of particle size in a Pd/C model catalyst on the kinetics of the H_2–D_2 exchange reaction. This study is the first to be carried out with a model catalyst prepared in situ in an ultra-high-vacuum system (UHV) and to use X-ray photoelectron spectroscopy to characterize the electronic energy levels within the palladium particles. Experiments were carried out by vacuum-depositing palladium particles on a carbon film of ~10 nm thickness, supported by a mica sheet. A two-chamber UHV apparatus permitted us to prepare the catalyst in one chamber and transfer it to a second reaction chamber without exposure to air. Both chambers of the vacuum system were bakeable at 200 °C and achieved background pressures of 10^{-9} torr. The sample preparation chamber was equipped with a metal evaporator and a quartz thickness monitor (Anelva, EVM-32 B). The reaction chamber, separated from the separation chamber by a greaseless stopcock, was equipped with a quadrupole mass spectrometer and a variable leak valve for introducing gas. The average size of the palladium particles was determined for each sample subsequent to the kinetics experiments, by removing the catalyst sample from the vacuum system and examining it with a transmission electron microscope (JEOL JEM-200 CX). Figure 1 shows a typical electron micrograph of this catalyst, in which one can see palladium particles ranging in size from the observation limit of 0.6 nm to approximately 2 nm. The surface area of the model catalyst system was always 10 × 10 mm or smaller.

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