Detection of H_3^+ in the Diffuse Interstellar Medium Toward Cygnus OB2 No. 12

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The molecular ion H_3^+ is considered the cornerstone of interstellar chemistry because it initiates the reactions responsible for the production of many larger molecules. Recently discovered in dense molecular clouds, H_3^+ has now been observed in the diffuse interstellar medium toward Cygnus OB2 No. 12. Analysis of H_3^+ chemistry suggests that the high H_3^+ column density (3.8×10^{14} per square centimeter) is due not to a high H_3^+ concentration but to a long absorption path. This and other work demonstrate the ubiquity of H_3^+ and its potential as a probe of the physical and chemical conditions in the interstellar medium.

The molecular ion H_3^+ is generally considered a fundamental molecule of interstellar chemistry, as it reacts efficiently with almost any neutral atom or molecule to initiate a network of ion-neutral reactions. It was suggested in the 1970s (*1*) that this network of reactions is responsible for producing molecules such as OH, CO, and H_2O, which not only serve as important astronomical probes but also play important roles in processes such as star formation.

The recent discovery of interstellar H_3^+ in dense molecular clouds toward the young stellar objects GL2136 and W33A (*2*), which are deeply embedded within the clouds, has provided direct observational evidence supporting the ion-neutral reaction scheme for the chemical evolution of molecular clouds. Subsequent observations have revealed the presence of abundant H_3^+ in many other dense clouds (*3*). Because of the simplicity of the H_3^+ chemistry, these observations provide direct estimates of the most fundamental properties of the clouds: number density, column length, and temperature.

In the course of carrying out this survey, we observed strong and broad H_3^+ absorption lines in the direction of the galactic center source GC IRS 3 (*4*). This finding suggested that H_3^+ is abundant not only in gravitationally bound dense clouds with high density ($n \sim 10^3$ to 10^5 cm^{-3}) but also in unbound diffuse clouds with low density ($\sim$10 to 10^3 cm^{-3}). To test this possibility, Cygnus OB2 No. 12 was observed, as this source is believed to be obscured largely by diffuse low-density clouds containing little molecular material (*5*). We report here the detection of a large amount of H_3^+ in the diffuse clouds in the direction of Cygnus OB2 No. 12.

Cygnus OB2 No. 12 (or VI Cygni 12) is the 12th member of the Cygnus OB2 association of young stars and was discovered in 1954 (*6*). This association is estimated to be 1.7 kpc (*7*) from Earth or about one-fifth of the distance to the center of the galaxy. The star Cygnus OB2 No. 12 suffers the largest extinction of any of the members of the association, $A_v \sim 10$, indicating that it has the largest column of absorbing material along its line of sight (*8*). On the basis of its extinction, distance, spectral type (B5), and luminosity class (Ie), the star Cygnus OB2 No. 12 is one of the most luminous stars in the galaxy (absolute visual magnitude ~ -10), more than a million times brighter than our sun (*9*).

Although Cygnus OB2 No. 12 suffers higher extinction than other members of its association, it is generally accepted that all the extinction occurs in a spatially patchy distribution of the interstellar dust (*5*). The absence of the 3.08-μm water ice absorption feature, associated with dense molecular clouds, and the presence of a 3.4-μm hydrocarbon feature (*5*), associated with diffuse interstellar gas, indicate that no dense molecular clouds occur along the line of sight. The identification of the gas with a circumstellar shell is rejected on the basis of a lack of excess infrared emission and the unusually strong stellar wind ($\sim$1400 km s^{-1}) of Cygnus OB2 No. 12 (*10*).

We detected two closely spaced lines of H_3^+ near 3.67 μm toward Cygnus OB2 No. 12 on 11 July 1997, using the CGS4 spectrometer at the United Kingdom Infrared Telescope (UKIRT) (*11*). A third line near 3.71 μm was detected on 17 September 1997 with the use of the Phoenix infrared spectrometer on the 4.0-m Mayall telescope of the Kitt Peak National Observatory (KPNO) (*12*). To further constrain the chemistry of the line of sight toward Cygnus OB2 No. 12, we also obtained spectra of CO (*13*).

The reduced H_3^+ spectra are shown in Fig. 1. The left portion of the figure, taken with CGS4, shows absorption of the $R(1,1)^+$ line of *para*-(*p*-)H_3^+ and the R(1,0) line of *ortho*-(*o*-)H_3^+. The right portion, obtained with Phoenix, shows absorption of the $R(1,1)^-$ line of *p*-H_3^+. The reduced CO absorption spectrum from CGS4 is relatively weak (Fig. 2). In dense molecular cloud sources, the fundamental CO lines are often saturated, so the relatively weak absorption toward Cygnus OB2 No. 12 suggests that the relative abundance of CO is much lower than in dense molecular clouds.

The amount of H_3^+ toward Cygnus OB2 No. 12 can be expressed as the column density $N(H_3^+)$, which can be defined as the integral of the H_3^+ number density (in molecules per cubic centimeter) along the line of sight $N \equiv \int [H_3^+] d\ell$. The equivalent width (or area) of an absorption line, $W_\lambda \equiv \int (1 - \frac{I}{I_O}) d\lambda$, taken from the spectrum can be related to the column density of the level N_{level} (for an optically thin line) by the standard equation $W_\lambda = (8\pi^3\lambda/3hc)\, N_{level} |\mu|^2$. In these formulas, $|\mu|^2$ is the square of the transition dipole moment (a measure of the inherent strength of the transition) (*14*), λ and I are the wavelength and intensity of the radiation, respectively, h is Planck's con-

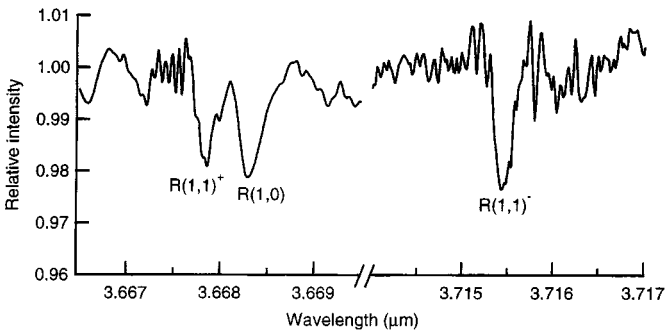

Fig. 1. Reduced spectra of Cygnus OB2 No. 12 in two wavelength intervals near 3.7 μm. The spectra were divided by spectra of the comparison star α Cygni and were wavelength calibrated with the use of atmospheric absorption lines. The left side contains two absorption lines of H_3^+ arising from the ground *para* and *ortho* states. The right side shows a single absorption from the ground *para* state. The high-frequency noise near 3.6675 μm is due to the removal of a strong CH_4 atmospheric line. Because the two spectra were obtained on different dates, they show different observed Doppler shifts.

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stant, and c is the speed of light.

Because the two p-H_3^+ lines R(1,1)$^+$ and R(1,1)$^-$ arise from the same energy level, the column densities N derived from the two should agree. The large discrepancy (Table 1) is most likely due to the effect of a strong (~45% deep) terrestrial line of CH_4 at 3.6675 μm, which was nearly coincident with the R(1,1)$^+$ line at the time of measurement. For the remainder of this discussion, we adopt a value for the H_3^+ column density of $N(H_3^+) = N_{ortho} + N_{para} = 3.8 \times 10^{14}$ cm^{-2}. From the CO spectrum (Fig. 2) we estimate a value of $N(CO) = 2 \times 10^{16}$ cm^{-2} (*15*).

To interpret the observed column densities of H_3^+ and CO, we developed a model of the H_3^+ chemistry of the interstellar medium (*16*). Using this model, we can extract $[H_3^+]$, L (the effective path length of the absorption), and $[\Sigma H]$ (the total number density of H atoms).

The molecular ion H_3^+ is formed by a two-step process: cosmic-ray ionization of H_2 to form H_2^+ and reaction of H_2^+ with H_2 to form H_3^+. Because the second step is faster than the first by many orders of magnitude, the formation rate of H_3^+ can be expressed as $\zeta[H_2]$, where ζ is the cosmic-ray ionization rate. There are two primary destruction paths for H_3^+: recombination with an electron and ion-neutral reaction with a neutral atom or molecule. The rate due to the former reaction is $k_e[e^-][H_3^+]$, where k_e is the rate constant for electron recombination and $[e^-]$ is the number density of electrons. The dominant ion-neutral destruction path for H_3^+ is assumed to be reaction with CO, with a rate of $k_{CO}[CO][H_3^+]$, where k_{CO} is the rate constant. If we assume a steady state, the rates of H_3^+ formation and destruction are equal, so that

$$\zeta[H_2] = k_e[e^-][H_3^+] + k_{CO}[CO][H_3^+] \quad (1)$$

Because not all of the number densities in this equation can be obtained by observations, some assumptions must be made to reduce the number of unknowns in this equation. First, we assume that all electrons in diffuse clouds come from ionization of atomic C to form C^+ (*17*), so that $[e^-] = [C^+]$. Second, we assume that all C is in the form of either C^+ or CO, so that $[\Sigma C] = [C^+]+[CO]$, where $[\Sigma C]$ denotes the total concentration of gaseous C atoms in any form (*18*). Third, we assume that nearly all H is in the form of H or H_2, so that $[\Sigma H] = [H] + 2[H_2]$.

To understand the meaning of Eq. 1, we introduce a parameter that represents the fraction of H in molecular form, $f \equiv 2[H_2]/[\Sigma H]$, or $[H_2] = (f/2)[\Sigma H]$. We also introduce a parameter that represents the fraction of C in molecular form $\alpha \equiv [CO]/[\Sigma C]$, so that $[CO] = \alpha[\Sigma C]$ and $[C^+] = (1-\alpha)[\Sigma C]$. Substituting these relations into Eq. 1 and solving for $[H_3^+]$ yields

$$[H_3^+] = \zeta\left(\frac{f}{2}\right)\left(\frac{[\Sigma H]}{[\Sigma C]}\right)\left(\frac{1}{k_e(1-\alpha) + k_{CO}\alpha}\right) \quad (2)$$

Note that the number density of H_3^+ does not depend on the absolute number density of the gas.

With the observed value of $N(H_3^+)$, one can determine the effective path length L of the absorption using the approximate relation $N(H_3^+) = [H_3^+]L$, which implies

$$L = \frac{N(H_3^+)}{[H_3^+]} = \left[\frac{2N(H_3^+)}{f\zeta}\right]\left(\frac{[\Sigma C]}{[\Sigma H]}\right) \cdot [k_e(1-\alpha) + k_{CO}\alpha] \quad (3)$$

Table 1. Observed H_3^+ lines and column densities derived from each line. Statistical uncertainties (3σ) are given in parentheses, but systematic errors are difficult to estimate and may be larger. Also listed are the Doppler velocities with respect to the local standard of rest v_{LSR} and the observed linewidths Δv (full width at half maximum). The uncertainty in the equivalent width (and column density) of the R(1,1)$^+$ line is large as a result of the effects of a nearly overlapping telluric CH_4 line. Rest wavelengths are from (*27*).

Transition	Rest wavelength (μm)	$\lvert\mu\rvert^2$ (D^2)	W_λ (μm)	N_{level} (cm^{-2})	Δv (km s^{-1})	v_{LSR} (km s^{-1})
R(1,1)$^+$	3.668084	0.0158	$3.9(9) \times 10^{-6}$	$1.6(4) \times 10^{14}$	17(5)	8(5)
R(1,0)	3.668516	0.0259	$5.4(9) \times 10^{-6}$	$1.4(2) \times 10^{14}$	22(5)	11(5)
R(1,1)$^-$	3.715478	0.0140	$5.2(7) \times 10^{-6}$	$2.4(3) \times 10^{14}$	16(3)	8(3)

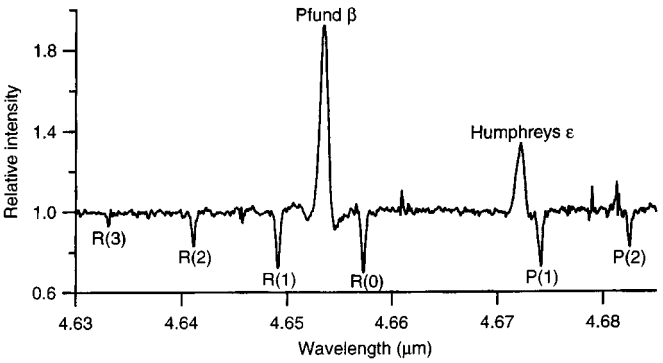

Fig. 2. Spectrum from 4.63 to 4.68 μm of Cygnus OB2 No. 12, showing R- and P-branch absorption lines of CO in the interstellar medium and emission lines of atomic H from the stellar atmosphere (Pfund β and Humphreys ε). The spectrum was divided by a spectrum of the comparison star γ Cygni and was wavelength calibrated with the use of atmospheric absorption lines.

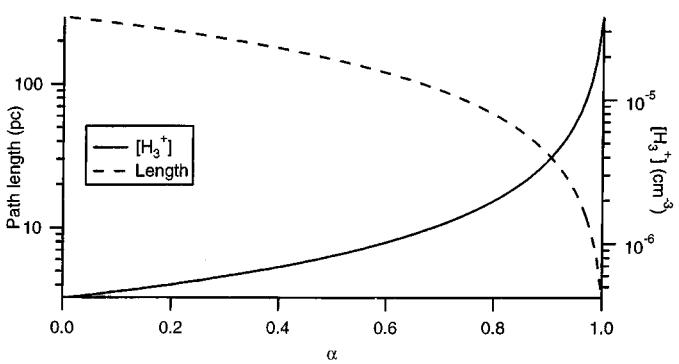

Fig. 3. Model results for the H_3^+ number density $[H_3^+]$ and the effective absorption path length L for Cygnus OB2 No. 12.

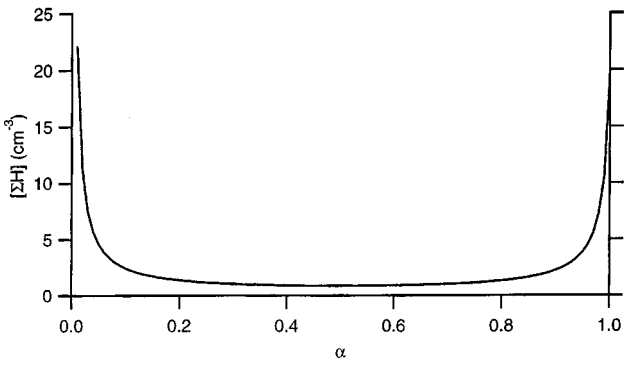

Fig. 4. Model results for the total number density of H atoms $[\Sigma H]$ for Cygnus OB No. 12.

To obtain an expression for the number density [ΣH], the definition of α can be rewritten as α = ([CO]/[ΣH])([ΣH]/[ΣC]). Substituting the approximate relation [CO]/[ΣH] ≅ N(CO)/N(ΣH) into this and solving for N(ΣH) gives

$$N(\Sigma H) = \frac{N(CO)}{\alpha}\left(\frac{[\Sigma H]}{[\Sigma C]}\right) \quad (4)$$

Equations 3 and 4 can be combined to derive an expression for the number density of the cloud

$$[\Sigma H] \cong \frac{N(\Sigma H)}{L} = \left[\frac{f\zeta N(CO)}{2\alpha N(H_3^+)}\right]\left(\frac{[\Sigma H]}{[\Sigma C]}\right)^2 \cdot \left[\frac{1}{k_e(1-\alpha) + k_{CO}\alpha}\right] \quad (5)$$

To determine [H_3^+], L, and [ΣH], we used $\zeta \sim 3 \times 10^{-17}$ s^{-1} (*19*), $f \sim 0.5$ (*20*), [ΣH]/[ΣC] ~ 10^4 (*21*), $k_e \sim 1.8 \times 10^{-7}$ cm^3 s^{-1} (*22*), and $k_{CO} \sim 2.0 \times 10^{-9}$ cm^3 s^{-1} (*23*). For N(H_3^+) and N(CO) we used our adopted observational values. The parameter α is difficult to estimate, and we leave it as a free parameter.

The resulting values of [H_3^+] and L for Cygnus OB2 No. 12 as a function of α (Fig. 3) show that, as α increases (more C is in molecular form) from 0 to 1, [H_3^+] increases from 4×10^{-7} to 4×10^{-5} cm^{-3} and L decreases from ~300 to ~3 pc. The limit α = 0 corresponds to the case where H_3^+ destruction is dominated by electron recombination (very diffuse clouds), and the limit α = 1 corresponds to the case where H_3^+ destruction is dominated by reaction with CO (very dense clouds).

The key parameter in these estimates (α) has not been determined, but, on the basis of observations and theoretical models of diffuse clouds (*17*), we infer that it is less than 0.1. From Fig. 3 we estimate [H_3^+] ~4×10^{-7} cm^{-3} and L ~300 pc. Unlike [H_3^+] and L, [ΣH] changes a lot for α < 0.1 (Fig. 4). From the visual extinction we can estimate N(ΣH), assuming the standard gas-to-dust ratio (*24*). If all of the extinction arises from the region where H_3^+ is observed (*25*), we estimate N(ΣH) ~ 2×10^{22} cm^{-2}. The calculated L ~ 300 pc then implies [ΣH] ~ 20 cm^{-3}.

Because H_3^+ undergoes constant chemical reactions with H_2 at a Langevin rate (*26*) and because there are no radiative transitions between *o*-H_3^+ and *p*-H_3^+, H_3^+ is in thermal equilibrium with H_2 in the cloud. By measuring the column densities of *o*- and *p*-H_3^+, one can estimate the kinetic temperature of the cloud. In thermal equilibrium, the ratio of the two states is given by the Boltzmann expression

$$\frac{N_{ortho}}{N_{para}} = \frac{g_{ortho}}{g_{para}} e^{-\frac{\Delta E}{kT}} = 2e^{-\frac{32.87}{T}} \quad (6)$$

where the g values are the statistical weights of the *o*- and *p*-H_3^+ states, ΔE is the energy difference between them, k is the Boltzmann constant, and T is temperature. Using the data in Table 1, we obtain an estimate of the cloud temperature of 27 K. This temperature is higher than the excitation temperature derived from the CO spectrum (Fig. 2), which is 10 K. This difference in temperatures may be reasonable because spontaneous emission will lower the excitation temperature of CO in diffuse clouds, where the collisional pumping to higher rotational states is slow as a result of the low number density.

These observations indicate that N(H_3^+) in the diffuse clouds toward Cygnus OB2 No. 12 (3.8×10^{14} cm^{-2}) is comparable to that of the dense clouds toward the young stellar objects GL2136 (4.0×10^{14} cm^{-2}) and W33A (6.0×10^{14} cm^{-2}) (*2*). This is not because of a higher number density [H_3^+] but because of a large effective path length L toward Cygnus OB2 No. 12, which may cross many diffuse clouds. Although large column densities of H_3^+ have been predicted in diffuse clouds (*17*), these calculations were based on a value of the H_3^+ electron recombination rate that has since been shown to be more than three orders of magnitude too low (*22*). This detection and analysis extend the diagnostic powers of H_3^+ to a new class of objects that are chemically quite different from dense molecular clouds and may allow us to gain further insight into the physical and chemical conditions of diffuse interstellar clouds.

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11. The UKIRT is operated by the Joint Astronomy Centre on behalf of the U.K. Particle Physics and Astronomy Research Council. CGS4 is a grating spectrometer for the region from 1 to 5 μm, currently incorporating a 256 by 256 InSb array. For details on the CGS4 spectrometer, see C. M. Mountain, D. J. Robertson, T. J. Lee, R. Wade, *Proc. Soc. Photo.-Opt. Instrum. Eng.* **1235**, 25 (1990).
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13. We observed the fundamental band of ^{12}CO near 4.66 μm in absorption on 1 August 1997 using CGS4 at UKIRT and also on 16 September 1997 using Phoenix on the 2.1-m telescope at KPNO. Millimeter-wave spectra of ^{12}CO (J = 2→1) and ^{13}CO (J = 2→1) were also obtained at the James Clerk Maxwell Telescope (JCMT) on 5 August 1997 and 13 November 1997, respectively. The JCMT is operated by the Joint Astronomy Centre on behalf of the U.K. Particle Physics and Astronomy Research Council, the Netherlands Organisation for Scientific Research, and the National Research Council of Canada. We obtained the CO measurements at the JCMT using the heterodyne receiver A2.
14. The values of |μ|^2 were provided to us by J. K. G. Watson.
15. This adopted value assumes that the CO lines are unsaturated and that the populations of the $J > 2$ levels are negligible. The measured equivalent widths are R(2) = 7.0×10^{-5} μm, R(1) = 1.3×10^{-4} μm, R(0) = 1.4×10^{-4} μm, P(1) = 1.3×10^{-4} μm, and P(2) = 7.2×10^{-5} μm. These values are uncertain by perhaps a factor of 2 because the atmospheric CO lines were nearly overlapping the interstellar CO lines at the time of measurement, causing the atmospheric correction to be quite imprecise. The line widths are ~20 to 30 km s^{-1}. The Doppler velocity with respect to the local standard of rest v_{LSR} (~15 km s^{-1}) of the CO lines is in rough agreement with the H_3^+ data, although the systematic uncertainty due to atmospheric interference is difficult to estimate.
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18. In diffuse clouds, models (*17*) indicate that atomic C is another abundant form of carbon. However, [C] can be included in [CO] in these expressions, as it has a similar Langevin rate constant for reaction with H_3^+, so it behaves just like CO with respect to H_3^+ chemistry.
19. The adopted value of ζ varies in the literature. We have adopted an average of the value $\zeta = 1 \times 10^{-17}$ s^{-1} used in model calculations of dense clouds [H.-H. Lee, R. P. A. Bettens, E. Herbst, *Astron. Astrophys. Suppl. Ser.* **119**, 111 (1996)] and the value $\zeta = 5 \times 10^{-17}$ s^{-1} used for diffuse clouds (*17*). We expect that further H_3^+ observations will lead to a better estimate of this important parameter.
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25. This assumption is supported by the currently available spectral data on Cygnus OB2 No. 12. The C_2 observations of R. Gredel and G. Münch [*Astron.*

Astrophys. **285**, 640 (1994)] show that at least 90% of the C_2 along this line of sight has v_{LSR} between ~6 and 15 km s^{-1}, whereas there is only a small component at v_{LSR} ~ 30 km s^{-1}. In addition, the K I spectroscopy of F. H. Chaffee Jr. and R. E. White [*Astrophys. J. Suppl. Ser.* **50**, 169 (1982)] shows evidence of K I absorption only near the observed velocity of H_3^+.

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Design of a Surface Alloy Catalyst for Steam Reforming

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Detailed studies of elementary chemical processes on well-characterized single crystal surfaces have contributed substantially to the understanding of heterogeneous catalysis. Insight into the structure of surface alloys combined with an understanding of the relation between the surface composition and reactivity is shown to lead directly to new ideas for catalyst design. The feasibility of such an approach is illustrated by the synthesis, characterization, and tests of a high–surface area gold-nickel catalyst for steam reforming.

Single crystal surfaces have long served as models of the active part of catalysts (*1*). Examples of catalyst design on the basis of fundamental, surface science–based insight are, however, extremely few. Recently, King and co-workers used a surface science approach to suggest new process conditions in which the effectiveness and stability of the usual Pt-based catalyst for the ammonia oxidation process can be markedly improved (*2*). Here we discuss an example in which the full step has been taken from atomistic surface science studies of model systems to the design of a high surface area alloy catalyst for the steam-reforming process. We present experimental results confirming the suggestion from a combination of scanning tunneling microscopy (STM), molecular beam scattering experiments, and density functional theory (DFT) calculations that Au alloyed into the surface layer of a Ni catalyst should increase the effectiveness of the catalyst in steam reforming.

In the steam-reforming process, hydrocarbon molecules (mainly CH_4) and water are converted into H_2 and CO. The usual catalyst for the reaction is based on Ni as the active element (*3*). The main problem with the reaction is that Ni also catalyzes the formation of graphite. Graphite formation impedes the activity and may eventually lead to a breakdown of the catalyst. One solution to this problem is to selectively poison the catalyst surface by adding H_2S to the reactants (*4*). Adsorbed S poisons the reforming process, but poisons the graphite formation to an even greater extent, so the net effect is an improved catalyst.

In a number of instances alloys have been shown to have superior catalytic properties (*5*) compared with elementary metals. In the past, research has focused on the class of binary metal systems that form ordered or random bulk alloys. Members of another class of two-component metal systems do not mix in the bulk. Even such metals may form stable alloys in the outermost surface layer (*6*, *7*). The Au/Ni system belongs to this category. The heat of solution of Au in Ni is large and positive (27 kJ/mol). Yet it has been found in STM studies by Nielsen *et al.* (*7*) that when Au is added to any of the low index Ni surfaces, an alloy is formed in the first atomic layer (Fig. 1). The Ni atoms in the surface layer are undercoordinated compared with the Ni atoms in the bulk. The Au atoms have an electron density that is more extended than that of the Ni atoms. When the Au atoms are alloyed into the surface layer, the neighboring Ni atoms experience a higher electron density or, equivalently, a higher effective coordination number. One can say that the Au atoms that are alloyed into the surface layer help in lowering the Ni surface energy (*7*).

The existence of this class of two-component bulk-immiscible metals that form surface alloys allows synthesis of materials in which the properties are changed selectively at the surface.

It is possible to use Au to modify the reactivity of Ni with respect to the steam-reforming process. As discussed above, two factors determine the suitability of a surface as a catalyst for this process: (i) the ability of the surface to activate hydrocarbon molecules and (ii) the tendency of the surface to bind C and form graphite.

As a measure of the ability of the surface to activate hydrocarbon molecules, we consider the energy barrier for abstraction of the first H atom from CH_4. For pure Ni catalysts, this is the rate-limiting step in the steam-reforming process (*8*). The effect of Au on the activation barrier was studied both theoretically and experimentally.

DFT calculations of the dissociation of CH_4 were performed by Kratzer *et al.* (*9*), who used a Ni slab with varying amounts of Au substituted into the surface layer to

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