# Equilibrium distributions of alkanes at a fixed partial pressure of molecular hydrogen

Robert A. Alberty

Gofuku, Toyama 930, Japan.

[1]H. Jones, *Modern Techniques of Microwave Spectroscopy*, edited by G. W. Chantry (Academic, New York, 1979), pp. 123–216.

[2]See for example, S. L. Coy, K. K. Lehmann, and F. C. DeLucia, J. Chem. Phys. **85**, 4297 (1986).

[3]T. Oka, *Molecular Spectroscopy: Modern Research*, edited by K. Narahari Rao (Academic, New York, 1976), Vol. II, pp. 229–253.

[4]T. Oka, *Advan. At. Mol. Phys.* **9** (Academic, New York, 1973), pp. 127–206.

[5]See for example, T. Amano and K. Tanaka, J. Chem. Phys. **83**, 3721 (1985).

[6]R. M. Lees and T. Oka, J. Chem. Phys. **51**, 3027 (1969).

[7]P. W. Daly and T. Oka, J. Chem. Phys. **53**, 3272 (1970).

[8]P. Langevin, Ann. Chim. Phys. **5**, 245 (1905).

[9]C. Gudeman, Thesis, University of Wisconsin (1982).

[10]S. Green, Astrophys. J. **201**, 366 (1975).

[11]J. C. Owrutsky, C. S. Gudeman, C. C. Martner, L. M. Tack, N. H. Rosenbaum, and R. J. Saykally, J. Chem. Phys. **84**, 605 (1986).

## NOTES

# Equilibrium distributions of alkanes at a fixed partial pressure of molecular hydrogen

Robert A. Alberty

*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139*

The three degrees of freedom for chemical reactions among hydrocarbons and molecular hydrogen in the gas phase are usually taken as $T$, $P$, and $H/C$, but there may be reasons for taking them as $T$, $P$, and $P_{C_2H_4}$ or $T$, $P$, and $P_{H_2}$. In order to discuss chemical equilibrium involving whole homologous series, it is convenient to use standard chemical thermodynamic properties of isomer groups,[1,2] since an isomer group in equilibrium can be treated as a single component. When the partial pressure of a reactant, such as ethylene or molecular hydrogen, is fixed, a Legendre transform can be used to define a new thermodynamic potential that is minimized at equilibrium.[3] However, in the case discussed here, the standard Gibbs energy of formation of an isomer group can be adjusted by considering the formation reaction.

Except for the first member or two of a homologous series, it has been found that the standard Gibbs energies of formation of the successive isomer groups in a homologous series can be represented by

$$\Delta_f G_n^0 = A + Bn, \tag{1}$$

where $n$ is the carbon number and $A$ and $B$ are functions of temperature only. Alberty and Oppenheim[4] showed that when the partial pressure of ethylene is fixed, the Gibbs energies of formation of the successive isomer groups are given by

$$\Delta_f G_n^* = a + bn, \tag{2}$$

where $a$ and $b$ are now functions of the temperature and the specified partial pressure of ethylene. Under these conditions, the successive isomer groups are pseudoisomers, and the mole fraction of the $n$th isomer group for the alkane homlogous series is given by

$$y_n = (1 - e^{-b/RT})e^{-(n-1)b/RT}, \quad n \geqslant 1. \tag{3}$$

Thus the equilibrium distribution is independent of $a$ (and $A$).

When the partial pressure of molecular hydrogen is fixed, the problem reduces to the polymerization of atoms, since molecular hydrogen is supplied to the extent needed. Smith and Missen[5] have treated this equilibrium polymerization for a finite number of polymers and show that at equilibrium

$$\mu_n = n\lambda, \tag{4}$$

where $\lambda$ is a Lagrange multiplier. Thus, the equilibrium chemical potentials of the $n$-mers are integer multiples of $\lambda$. When the partial pressure of molecular hydrogen is fixed, the formation reaction for an alkane isomer group can be written

$$n\mathrm{C(graphite)} + (n+1)\mathrm{H_2}(g, P_{H_2}) = \mathrm{C}_n\mathrm{H}_{2n+2}(g, P_{hc}), \tag{5}$$
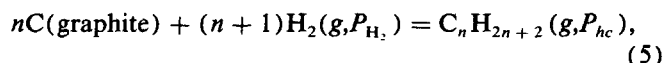
where $P_{hc}$ is the total pressure of hydrocarbons in the system. The Gibbs energy of formation of the isomer group under these conditions is

$$\Delta_f G_n^* = \Delta_f G_n^0 + RT \ln (P_{hc}/P^0)$$
$$- (n+1)RT \ln (P_{H_2}/P^0)$$
$$= a + bn, \tag{6}$$

where $P^0$ is the reference pressure (1 bar) and

$$a = A + RT \ln [(P - P_{H_2})/P^0] - RT \ln (P_{H_2}/P^0), \tag{7}$$

$$b = B - RT \ln (P_{H_2}/P^0). \tag{8}$$

($a$ is now a function of $T$, $P$, $P_{H_2}$.) The chemical potential of the $n$th isomer group at equilibrium is given by

$$\mu_n = \Delta_f G_n^* + RT \ln y_n = a + bn + RT \ln y_n, \tag{9}$$

where $y_n$ is the equilibrium mole fraction within the alkanes. Thus, from Eq. (4),

$$\sum_{n=1}^{\infty} y_n = 1 = \sum_{n=1}^{\infty} [\exp(-a/RT)]\{[\exp(\lambda/RT)]$$
$$\times [\exp(-b/RT)]\}^n$$
$$= [\exp(-a/RT)] \sum_{n=1}^{\infty} x^n, \qquad (10)$$

where $x = [\exp(\lambda/RT)][\exp(-b/RT)]$. Equation (10) is useful for calculating equilibrium distributions only when the series converges; that is when $x < 1$. Under these conditions, Eq. (10) becomes

$$[\exp(-a/RT)]x/(1-x) = 1 \qquad (11)$$

and

$$x = 1/[1 + \exp(-a/RT)]. \qquad (12)$$

The equilibrium mole fractions are given by the successive terms in Eq. (10) so that

$$y_n = [\exp(-a/RT)]x^n. \qquad (13)$$

Under conditions where $a = 0$, $y_n = (1/2)^n$. As $a$ decreases from zero, $x$ rapidly becomes smaller and alkanes with high carbon numbers are not formed to an appreciable extent. As $a$ increases from zero, $x$ approaches unity. Thus as the partial pressure of hydrogen is reduced, the averge carbon number at equilibrium becomes larger. Polymerization to an infinite extent is also encountered when the alkanes are formed at constant ethylene partial pressure.[4] Note that the equilibrium distribution at constant ethylene partial pressure depends only on $b$ (that is, on $B$ and $P_{C_2H_4}$), but the equilibrium distribution at constant hydrogen partial pressure depends only on $a$ (that is, on $A$, $P$, and $P_{H_2}$).

[1] R. A. Alberty, I&EC Fund. 22, 318 (1983).
[2] R. A. Alberty and C. A. Gehrig, J. Phys. Chem. Ref. Data 13, 1173 (1984).
[3] R. A. Alberty and I. Oppenheim, J. Chem. Phys. 89, 3689 (1988).
[4] R. A. Alberty and I. Oppenheim, J. Chem. Phys. 84, 917 (1986).
[5] W. R. Smith and R. W. Missen, Chemical Reactions Equilibrium Analysis (Wiley, New York, 1982).

# The Stark effect in the $B\,^3\Pi$–$X\,^3\Delta$ band system of TiO

Timothy C. Steimle and Jeffrey E. Shirley

*Department of Chemistry, Arizona State University, Tempe, Arizona 85287-1604*

Theoretical bonding models[1,2] suggest that there are two general features associated with the first row transition metal (TM)–oxygen bond. There is an invariant ionic charge distribution and there is the formation of TM $d$ and O $2p$ covalent bonds. The propensity for covalent bond formation is countered by an increase in $d$-$d$ exchange energy. There is a direct correlation between these two features and the TM $3d^n4s^2$ and $3d^{n+1}4s$ occupation. Therefore, when both contributions are present a multireference configuration description of the wave function is required. CuO is expected to have nearly purely ionic bonding and be adequately described by a single configuration wave function. At the middle of the row, where there is balance between the exchange energy and bond formation, the wave functions are not expected to be well represented by a single configuration. Accordingly, obtaining wave functions accurate enough to predict physical properties requires a very sophisticated level of computation.[3] At the left hand side of the first row transition metals (Sc or Ti) where the covalent bonding is stronger than the $3d$-$3d$ exchange, a single configuration description is again expected to be reasonable.

The permanent electric dipole moment $\mu$ is an effective measure of the ionic bonding character and should be among the most accurately predicted molecular properties. In addition, $\mu$ is the primary factor governing the interaction of radiation with matter. In a continuing study of first row transition metal monoxides (CuO,[4] FeO,[5] and CrO[3]), we have measured $\mu$ for $^{48}$Ti$^{16}$O in its ground ($X\,^3\Delta_1$) state using a sub-Doppler optical technique.

Owing partly to its prevalence in the spectra of stars, the data base for TiO is extensive.[6] The strong visible absorption is due to the $\gamma(B\,^3\Pi$–$X\,^3\Delta)$ band system which has been recorded in emission at high resolution and analyzed to obtain
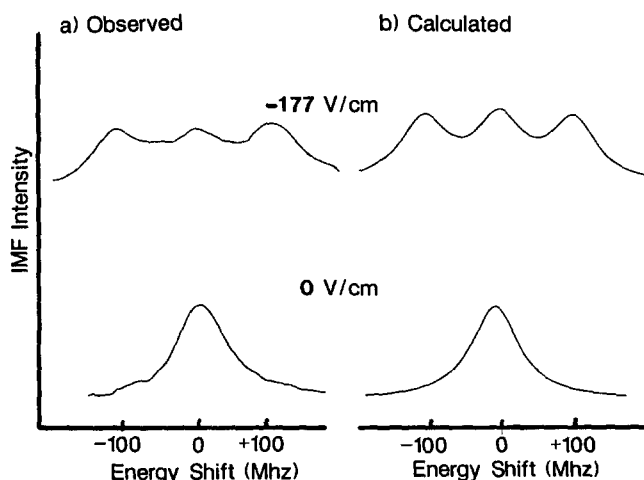


FIG. 1. The $^Q Q_{11a}$ (1) branch feature ($\nu = 16\,227.020$ cm$^{-1}$) of the $\gamma(B\,^3\Pi_0$–$X\,^3\Delta_1)$ band system recorded at sub-Doppler resolution as a function of dc electric field. (a) Observed. (b) Calculated.