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Ab initio 6-31G** electronic structure calculations have been used to determine the minimum energy geometries and vibrational frequencies of molecular clusters of water and carbon dioxide. Application of statistical thermodynamics leads to theoretical equilibrium constants for gas phase dimerization of water and the formation of an adduct of carbon dioxide with water. The low energy vibrations of the clusters lead to much larger contributions to the vibrational partitioning of the energy than do the fundamental vibrations of the monomeric species. A new "Harmonic-Morse" formula is derived to estimate anharmonicity from optimized harmonic frequencies and two additional values on the potential surface for each vibration. These *ab initio* calculations of equilibrium constants are very close to recent measurements and fall within the range of values obtained by other methods. This no-parameter treatment gives excellent agreement for the equilibrium of H₂O–CO₂ near the supercritical fluid range of CO₂ and suggests that a "Theory of Significant Clusters" may be extended to a model of supercritical fluids which includes the effects of anharmonicity.

I. INTRODUCTION

The statistical thermodynamical formulation of equilibrium constants for gas phase reactions has been readily available in a number of texts[1,2] for many years. However, the major barrier to practical application of these well known equations is the need to know the vibrational frequencies of all the species in the reaction. Even if one uses the extensive JANAF Thermochemical Tables[3] for the reactant species, there is still a need to know the additional frequencies created when a cluster is formed.

New vibrations caused by the formation of a weakly bound cluster of monomers are typically a few hundred wave numbers which then appear as a negative exponent in the vibrational partition function. Thus, these low energy vibrations have much larger numerical importance than do the terms caused by vibrations in true chemical bonds, which typically have energies of several thousand wave numbers.

Weak interactions need to be treated accurately if a statistical thermodynamics approach is used to calculate the equilibrium constant. The importance of these low-frequency modes was demonstrated recently in a proof-of-concept paper[4] based on the Ph.D. thesis of Nguyen.

There are really two problems related to the use of calculated vibrational frequencies. First, the frequencies are often 15%–20% too high.[5] This is due to limitations in basis set completeness and less than full configuration interaction treatment of the electronic wave function. Second, the harmonic force field may be inadequate for weak interactions. There is a need to introduce anharmonicity corrections. Hess, Schaad, Carsky, and Zahradnik's[5] review indicates that anharmonicity correction is easy for diatomics, but there is still a need for a way to introduce anharmonicity in the polyatomic case. This work provides a new "Harmonic-Morse" approach which includes anharmonicity into polyatomic vibrations based on a fully optimized harmonic force field calculation. The success of this new approach may be judged from the results obtained for a full statistical thermodynamic treatment of two equilibria involving weak interactions (1) hydrogen bonding in the case of water dimerization; (2) Lewis-donor–acceptor interactions in water and carbon dioxide.

II. METHOD

The GAMESS electronic structure program[6] was used with a 6-31G** basis set[7] at the single-determinantal level to optimize the geometry of H₂O, CO₂, H₂O–H₂O, H₂O–CO₂ and to compute the vibrational frequencies in the harmonic approximation. The geometries were exhaustively optimized to a maximum gradient of 0.000 001 hartree/bohr. This fully optimized the harmonic force field, and the harmonic frequencies values were computed directly with no scaling. The optimized geometry was in excellent agreement with the experimental intermolecular distance measured by Dyke and Muenter[7] and the water–carbon dioxide complex agreed with the overall shape reported by Peterson and Klemperer[8] as shown in Table I. Tables II and III may be used to check results presented later. Uniform scaling of the calculated vibrational frequencies[10] was also carried out. The results are shown below.

The main effort of this work is to determine the accuracy of equilibrium constants calculated at the 6-31G** single-determinantal level without use of any empirical adjustments. The moment-of-inertia tensor was set up using the atomic coordinates determined from the optimization. The tensor was diagonalized and the moments about the principal axes were obtained to be used in the rotational partition functions. Simple expressions were used for the translational partition functions with the masses of the average natural abundance atomic weights. A straightforward program was then written in the notation of McQuarrie[2] to compute the full expression for K_p using results from the GAMESS program output. These expressions have been known for many years, but vibrational frequencies are necessary to evaluate K_p.

Here we test the concept of "Significant Clusters" ap-

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TABLE I. *Ab initio* calculations for H_2O–H_2O and H_2O–CO_2.

		H_2O–H_2O	H_2O–C_2O
R^a (Å)	Calc.	2.9802	2.7820
	Expt.	2.98±0.01[b]	2.836[c]
E_{total} (a.u.)		−152.0560	−263.6699
ΔE_{vib} (kcal/mol)		3.5576	2.6556
$E_{binding}$ (kcal/mol)		−5.5270	−3.2630

[a]R: R_{O-O} for H_2O–H_2O. R_{C-O} for H_2O–CO_2 and R_{C-C} for CO_2–CO_2, respectively.
[b]T. R. Dyke and J. S. Muenter, J. Chem. Phys. **60**, 2929 (1974).
[c]K. I. Peterson and W. Klemperer, J. Chem. Phys. **80**, 2439 (1984).

plied to *gas clusters* based on the Eyring–Jhon "Theory of Significant Liquid Structures."[4,11] We also investigated application of the low pressure formulation to the case of H_2O–CO_2 at 1 atm pressure for temperatures between the boiling point of H_2O and the sublimation point of CO_2. The success of this simple case may lead to future extension in a study of H_2O in supercritical fluid CO_2.

The concentration equilibrium constant K_c and the partial pressure equilibrium constant K_p of the reaction can be written in terms of the partition functions q_i, where N_i is the number of particles in the canonical ensemble. This can be related to a stoichiometric coefficient n in the reaction equation by multiplying n by Avagadro's number,

$$Q(N,V,T) = \frac{[q(g)]^{N(g)}}{N(g)!} . \tag{1}$$

Here, $Q(g)$ is the canonical ensemble partition function of a product $N(g)$ cluster, and $q(g)$ is the partition function for a single g-mer cluster. Note that g-clusters are of the same species and mixed clusters are treated here. Rushbrooke[12] has shown that *the total partition function can be factored as long as a reversible, sequential addition process can be used to build the final cluster from its constituents.*

This "build-up process" is rigorously true when one considers the cases of a single molecule colliding (and reacting) with another monomer, a dimer of the same species, or

TABLE II. Coordinates of H_2O–H_2O and H_2O–CO_2 (Å).

		X	Y	Z
H_2O–H_2O				
	H	1.053 406	0.145 143	0.000 860
	O	0.127 567	−0.056 414	0.000 404
	H	−0.317 605	0.774 257	0.000 501
	H	3.407 186	−0.160 809	−0.753 798
	O	3.085 779	0.305 062	0.001 713
	H	3.406 631	−0.161 384	0.757 107
H_2O–CO_2				
	H	0.756 874	0.000 000	−0.612 823
	O	0.000 000	0.000 000	−0.050 386
	H	−0.756 874	0.000 000	−0.612 823
	O	1.143 390	0.000 000	2.758 561
	C	0.000 000	0.000 000	2.731 670
	O	−1.143 390	0.000 000	2.758 561

TABLE III. Calculated moments of inertia (10^{-39} erg s²).

	I_a	I_b	I_c
H_2O	0.0958	0.1898	0.2856
CO_2	0.0000	0.0000	6.9430
H_2O–H_2O	0.3810	13.6420	13.6430
H_2O–CO_2	7.1364	17.5070	24.6430

even a single molecular adduct such as CO_2–H_2O. This is the main principle of the recently adapted "Significant Structure Theory of Clusters" from Eyring and Jhon[11] to gas phase clusters by Nguyen et al.[4]

Contributions to each species partition function $q(g)$ can also be factored to include translation q_t, rotation q_r, vibration q_v, electronic energy q_e, and nuclear energy q_n. Therefore, $q(g)$ can be written as follows:

$$q(g) = q_t(g)q_r(g)q_v(g)q_e(g)q_n(g). \tag{2}$$

The electronic partition function is as follows:

$$q_e(g) = \omega_{e1} e^{D_e/kT}. \tag{3}$$

Here, $(-D_e)$ is the energy of the ground electronic state (at the 6-31G** level), $q_n(g)=1$ excluding nuclear excitations and ω_{e1} is the degeneracy of the electronic ground state which is also 1 here since all species are ground state singlets. The formula of the cluster partition function $q(g)$ is obtained upon substitution of q_t, q_r, q_v, and q_e into $Q(N,V,T)$ as Eq. (4),

$$q(g) = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_A \Theta_B \Theta_C}\right)^{1/2}$$
$$\times \left(\prod_{j=1}^{3n-6} \left\{ \frac{\exp\left(\frac{-h\nu_j}{2kT}\right)}{\left[1-\exp\left(\frac{-h\nu_j}{kT}\right)\right]} \right\} \right) \omega_{e1} e^{D_e/kT}. \tag{4}$$

Here, σ is the rotational symmetry number of the g-cluster and Θ_r is the rotational temperature; $r=A,B,C$; and $I_r=I_A$, I_B, I_C, are the principal moments of inertia. Note in the vibrational partition function $(-h\nu_j/kT)$ is negative, and the contribution of each mode to q_v is greater as the frequency is lower. Thus, new frequencies resulting from interaction between molecules in clusters are very important in calculating the vibrational partition function.

The equilibrium constant K_p can then be expressed in terms of partition functions. For a general chemical reaction

$$n_A A + n_B B \rightleftharpoons n_C C + n_D D. \tag{5}$$

Assuming a mixture of ideal gases, the partition function of the system is a product of the partition functions of the individual components,[1,2,12]

$$Q(N,V,T) = \prod_i^N Q(N_i,V,T) = \prod_i^N \frac{q_i(V,T)^{N_i}}{N_i!} . \tag{6}$$

Here, $i=A,B,C$. We have

$$\ln K_c(T) = \sum_i^N n_i \ln\left(\frac{q_i}{V}\right). \tag{7}$$

K_c is the concentration equilibrium constant of the reaction. Also, N_i is taken to be positive for products and negative for reactants. For an ideal gas system (up to about 2 atm pressure here because of the nonideal behavior of CO_2), K_p can be expressed in terms of partial pressures, then

$$K_p(T) = (kT)^{\sum_i^N n_i} K_c(T). \tag{8}$$

Thus the equation of the equilibrium constant is obtained under low pressure gas phase conditions.

Next consider whether such a formulation is applicable to the case of gaseous CO_2 in equilibrium with H_2O vapor below the boiling point of liquid water. Note that the Eyring–Jhon "Significant Structure Theory of Liquids"[11] was quite successful in prediction of the properties of liquid water and heavy water.[13] It was suspect because the vibrational partition function used frequencies taken from solid ice and monomeric water vapor. This work uses calculated vibrational frequencies for the "Significant Clusters" and applies the gas phase equations to data on vapor equilibria. A new method is derived in the Appendix for the inclusion of anharmonicity effects.[14,15] This study of the low pressure equilibrium forms a basis for future study of the effect of water on the supercritical fluid state of CO_2. Thus, we tested the "Significant Structure of Clusters"[4] for application to fluids in the spirit of the Eyring–Jhon "Significant Structure Theory of Liquids"[11] by assuming the partition function of the vapor is given by an equilibrium of "Significant Structures" as

$$q = (q_{CO_2})^A (q_{g-H_2O})^B \prod_{i=1}^n [q_{(H_2O)_n CO_2}]^{Ni} \tag{9}$$

and $n=1$. In order to compare to data for H_2O in CO_2 at 1 atm pressure above the sublimation temperature of CO_2, the simple cluster of H_2O–CO_2 may be the most significant cluster. Seen below, this gives good agreement with experiment even up to 60 atm pressure and implies this is the dominant cluster. Future work may refine this treatment to include larger clusters as indicated in Eq. (10),

$$(H_2O)_n + (CO_2)_m \rightleftharpoons (H_2O)_n - (CO_2)_m, \tag{10}$$
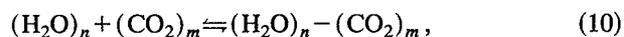
$$K_C = \frac{C_{(H_2O)_n (CO_2)_m}}{[C_{(H_2O)_n}][C_{(CO_2)_m}]}. \tag{11}$$

The K_p of $(H_2O)_n$–$(CO_2)_m$ can be obtained from K_c of $(H_2O)_n$–$(CO_2)_m$ using Eqs. (8) and (11), assuming ideal gas behavior. Here n and m are restricted to only one significant structure ($n=m=1$). It is then possible to calculate the thermodynamic properties of CO_2–H_2O vapor using this simple significant structure theory. Inclusion of $(H_2O)_2$–CO_2, H_2O–$(CO_2)_2$, etc., may be necessary at higher supercritical pressures. However, this requires estimation of mole fractions of such species by searching for shallow local minima in the Helmholtz free energy hypersurface.[11] Larger clusters of $(H_2O)_n$–$(CO_2)_m$ may also require a partition function

TABLE IV. Thermodynamic properties of H_2O–H_2O and H_2O–CO_2.

		K_p (1/atm)	ΔG (kcal/mol)	ΔH (kcal/mol)[c]	ΔS (e.u.)
H_2O–H_2O [d]					
Calc.	SCF	0.009	3.48	−3.61	−19.00
	Scaled	0.014	3.16	−4.67	−20.97
	(Morse)$_1$	0.009 2	3.48	−3.55	−18.85
	(Morse)$_{15}$	0.009 2	3.48	−3.27	−18.10
Expt.[a]		0.011 0	3.34	−3.63	−18.61
H_2O–CO_2 [e]					
Calc.	SCF	0.007 6	2.89	−2.28	−18.34
	Scaled	0.001 9	2.63	−4.15	−22.75
	(Morse)$_1$	0.007 65	2.89	−2.11	−16.77
	(Morse)$_{15}$	0.007 60	2.89	−2.91	−19.45
Expt.[b]		0.008	2.94	−4.80	−25.9

[a]L. A. Curtiss et al., Chem. Phys. Lett. **54**, 575 (1978).
[b]C. R. Coan and A. D. King, J. Am. Chem. Soc. **93**, 1857 (1971).
[c]ΔH is computed by the formula $\Delta H = \Delta E_{binding} + \Delta E_{vib} - 4RT$.
[d]Data at 373 K.
[e]Data at 298 K.

which includes the nonideal behavior of CO_2 and H_2O at supercritical pressures. Nguyen et al.[4] used an expression which included an accurate empirical fit to the vapor pressure of the bulk material. This may be necessary for even more precise treatment of supercritical fluid CO_2 containing H_2O. However, this work emphasizes a completely nonempirical (no parameters) treatment of equilibrium constants using the "Significant Cluster" concept, without any correction for nonideal behavior of either bulk H_2O or bulk CO_2.

III. RESULTS AND DISCUSSION

Using direct comparison to experimental data, the first case is the gas phase thermal conductivity measured by Curtiss, Frurip, and Blander[16] which is given at four temperatures (358.4, 367.1, 375.9, and 386.4 K) near the boiling point of water. They found that the primary measurements could be accounted for by including only monomeric water and <4% of dimers without any other species. This is a clear cut application for the use of only the "Significant Structures" of the monomer and dimer structures found using the GAMESS program. Table IV shows results for 373 K and their estimated experimental uncertainty is 1% absolute error. Note that previous measurements of the enthalpy of association from measurement of the second virial coefficient[17–19] range from about −3.0 kcal/mol to about −5.7 kcal/mol. Therefore the values of −3.61, −3.55, and 3.27 kcal/mol obtained from the plots of the "Significant Cluster" $\ln(Kp)$ vs $(1/T)$ are all in excellent agreement with experiment. Using the average atomic masses and harmonic vibrational frequencies without scaling, the computed values of K_p, Gibbs free energy and enthalpy of formation are within 17% without any parameters.

The anharmonicity correction applied through the "Harmonic-Morse" formula (Appendix) made the most improvement in the computed entropy of association. Apparently, the ability of the vibrational partition function to describe larger geometrical distortions is due to the use of the anharmonic Morse potential. This improved the entropy cal-

culations more than the quantities which depend primarily on simple energy differences at the bottom of the energy wells.

Although GAMESS provides multiconfigurational capability, the computer memory required exceeded that available on the workstation (24 Mb) used in this work. The hydrogen bonding in the dimer is undoubtedly highly anharmonic in vibrational levels above the lowest level used here to sum over higher multiples in the vibrational partition function. In addition, only the lowest energy dimer geometry (Table II) was used here. Another dimer geometry is possible[4] which permits a metastable energy form to participate in the "randomness" of the dimer. Thus, the Gibbs free energy and the enthalpy are given in reasonable agreement mainly due to direct energy differences. Additional randomness does show up in the experimental entropy due to additional states not included in this simple model.

The precedent of Eyring–Jhon "Significant Structures" in liquids and the great interest in supercritical fluid CO_2 (Ref. 20) prompts a comparison to data obtained by Coan and King[21] for water vapor in compressed CO_2. These data ranged over pressures from 1–60 atm and temperatures from 25–100 °C compared to the critical temperature of 31.05 °C and a critical pressure of 72.8 atm for CO_2.[18] The "Significant Cluster" partition functions depend on gas phase concepts. Therefore, a supercritical fluid may be more suited to this analysis than a true liquid at a temperature below the atmospheric boiling point. While high pressure can force molecules in a gas to be almost as near together as in a liquid, temperatures above the normal boiling point provide sufficient energy to populate higher translational, rotational, and even vibrational states than is the case below the boiling point at 1 atm pressure. Thus, the "Significant Cluster" concept should be valid to varying degrees in vapors and even supercritical fluids.

In Table VI the calculated K_p value for one molecule of H_2O combining with a single molecule of CO_2 compares favorably with the measured (reciprocal) value of H_2O dissolved[21] in gaseous CO_2. The Gibbs free energy of formation is in excellent agreement with the measured value. Reasonable agreement is obtained for the entropy of association. Here the deviation shows up in the enthalpy of association. In this case there is only one clear geometry for the complex of H_2O–CO_2,[8] so the main uncertainty is probably due to the single-determinantal treatment of the electronic wavefunction. In such a weakly bound complex, the correlation energy effect becomes a much larger fraction of the total binding energy and other electronic configurations may be important. Efforts to carry out multiconfigurational treatment of the vibrational frequencies proved to be just slightly beyond available workstation memory and disk space. Note that scaling all the vibrational frequencies by a uniform factor[10] of 0.89 actually made the agreement with experiment worse than direct use of the self-consistent field (SCF) harmonic frequencies.

It is interesting that the experimental binding Gibbs free energy values in Table IV indicate very good agreement with experiment. This was the case even though the H_2O–CO_2 complex has a larger enthalpy change than $(H_2O)_2$, while the calculated electronic binding energies indicate the reverse
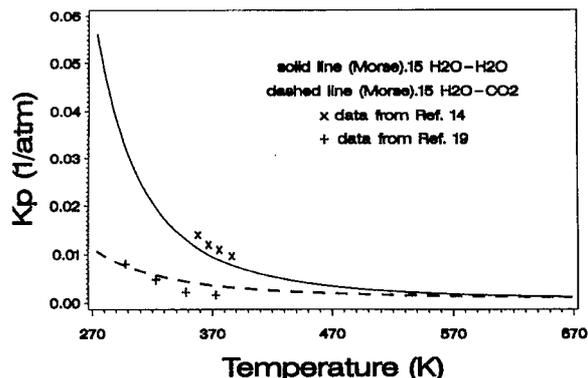

FIG. 1. Plot of the "no-parameter" equilibrium constant compared to experiment.

order in Table I. Coan and King[21] found *two* cross-virial interactions in their data. They interpreted this in terms of one "physical" interaction and another "chemical" interaction between H_2O and CO_2. Since the van der Waals complex used here[8] as a "Significant Structure" did not form H_2CO_3 and the calculated binding energy is too small, it seems that under 1:1 conditions the "physical" interaction is the van der Waals complex used here. At higher concentrations of H_2O (perhaps as H_2O–H_2O–CO_2) a true chemical rearrangement to H_2CO_3 may occur so that the experimental binding energy of −4.80 kcal/mol may be the effect of *both* van der Waals complex formation and a true chemical reaction to form H_2CO_3.

Another uncertainty is the basis set superposition error (BSSE) due to formation of a supermolecule from two smaller molecules using an incomplete basis set. Recent work on the cyclic form of the hydrogen peroxide dimer $(H_2O_2)_2$ by Dobado and Molina,[23] using the same 6-31G** basis set as here, found a BSSE value of 1.40 kcal/mol out of a total binding energy of −6.75 kcal/mol for *two hydrogen bonds*. Thus, even the good agreement of the calculated binding energy for the water dimer in Table IV is uncertain by about 0.7 kcal/mol for a single hydrogen bond with perhaps a larger BSSE for the H_2O–CO_2 complex since the CO_2 portion of the complex includes d orbitals which might be used by the H_2O portion to lower the energy further. However, Jackels and Phillips[24] noted in their study of hydroxy and hydroperoxy radicals that the 6-31G** basis generally produces calculated dissociation energies which are too small by about 5%–15% (cf. Ref. 24, p. 5017).

With these uncertainties in the binding energies of about 1 kcal/mol out of some 4 kcal/mol, this no-parameter work chooses to proceed with the calculated values and use K_p shown in Fig. 1, and Table IV as the "merit-value" of the overall agreement with experiment because it derives directly from the Gibbs free energy which contains a "balance" between enthalpy and entropy effects. Thus the Harmonic-Morse frequencies described in the Appendix are given in Tables V and VI compared to scaled and unscaled harmonic frequencies. In our judgement, the merit-value of K_p in Table IV indicates that Harmonic-Morse frequencies based on a finite step size of 15% in the normal (harmonic)

TABLE V. Calculated vibrational frequencies for H_2O–H_2O.

VIB_{SCF} [a]	$VIB_{0.89}$ [b]	$(VIB_M)_{0.1}$ [e]	$\Delta\omega_1$ [c]	$(VIB_M)_{0.15}$	$\Delta\omega_2$ [d]	VIB_{Expt} [f]
4256	3787	3898	−1	3886	−13	3899
4238	3772	3884	3	3871	−10	3881
4142	3686	3803	7	3793	−4	3797
4100	3649	3768	50	3757	39	3718
1797	1600	1735	66	1734	65	1669
1767	1573	1707	54	1707	54	1653
612	545	605		605		
377	335	374		374		
177	158	176		176		
143	127	143		143		
138	123	137		137		
117	104	117		117		

[a] VIB_{SCF} are the calculated vibrational frequencies by the SCF method.
[b] $VIB_{0.89} = 0.89 \times VIB_{SCF}$.
[c] $\Delta\omega_1 = (VIB_M)_1 - VIB_{Expt}$.
[d] $\Delta\omega_2 = (VIB_M)_{15} - VIB_{Expt}$.
[e] VIB_M are the corrected frequencies by MORSE potential function.
[f] The experimental data of the water dimer, L. Fredin, B. Nelander, and G. Ribbegard, J. Chem. Phys. **66**, 4065 (1977).

coordinate give best agreement with experiment. Tables V and VI indicate *nonlinear scaling* of harmonic frequencies [Appendix, Eq. (A13)] gives better agreement with known experimental frequencies,[25–28] but the accuracy of the low energy frequencies can only be inferred from the computed K_p values. Since uniform scaling of the harmonic frequencies by 0.89 actually produced K_p values in worse agreement with experiment than the unscaled frequencies, it may be that the very low frequencies should not be scaled as much as the higher frequencies. Although the low frequencies are not known, the Harmonic–Morse correction seems to improve the computed K_p value. Further study is indicated for extensive evaluation of the nonlinear Harmonic–Morse frequency correction. However, it should be clear that this data is a fair comparison to a large data base of compounds in Ref. 10 using a 6-31G** basis and direct comparison to experimental frequencies in Refs. 25–28. Furthermore, the Harmonic–

TABLE VI. Calculated vibrational frequencies for H_2O–CO_2.

VIB_{SCF} [a]	$VIB_{0.89}$ [b]	$(VIB_M)_{0.1}$ [c]	$\Delta\omega_1$ [d]	$(VIB_M)_{0.15}$	$\Delta\omega_2$ [e]	VIB_{Expt} [f]
4270	3800	4152	427	3954	229	3725
4151	3694	4040	408	3853	221	3632
2583	2299	2540	189	2468	117	2351
1762	1568	1742	144	1709	110	1598
1516	1349	1501	116	1477	92	1385
753	670	749	84	743	78	665
739	658	736	64	720	64	656
213	190	213		213		
157	139	157		156		
115	102	115		115		
52	46	52		52		
48	43	48		48		

[a] VIB_{SCF} are the calculated vibrational frequencies by the SCF method.
[b] $VIB_{0.89} = 0.89 \times VIB_{SCF}$.
[c] VIB_M are the corrected frequencies by the Morse potential function.
[d] $\Delta\omega_1 = (VIB_M)_1 - VIB_{Expt}$.
[e] $\Delta\omega_2 = (VIB_M)_{15} - VIB_{Expt}$.
[f] The experimental data of H_2O–CO_2; L. Fredin, B. Nelander, and G. Ribbegard, Chem. Scr. **7**, 11 (1975).

Morse formula (A13) does not depend on single-determinantal energy surfaces. The formula may be applied to frequencies derived from multiconfigurational SCF (MC-SCF), configuration interaction (CI), or other methods including electron correlation which use the harmonic normal mode analysis.

IV. CONCLUSIONS

A completely *ab initio* set of equations has been given to apply a no-parameter treatment of "Significant Clusters" to vapor phase equilibria which border on the conditions necessary for water vapor in supercritical fluid CO_2.[20] Standard single-determinantal 6-31G** vibrational frequencies of small molecular clusters were used with "Harmonic–Morse" anharmonicity correction to eliminate any parameterization at the level of the vibrational partition function (the SCF harmonic frequencies are high compared to experimental values[3,25–28]). The vapors were treated as ideal gases. The full partition function form of the equilibrium constants using only natural abundance atomic masses produced agreement within 21% of K_p for water vapor at 373 K and within 5% of K_p for water vapor in equilibrium with carbon dioxide at 298 K. This suggests statistical thermodynamics of "Significant Clusters" may be a good model of supercritical fluids once a full quantum level spectrum is available for the predominant molecular species.

One of the most interesting results is that the usual practice of scaling the vibrational frequencies (Table II) by a factor[10] of 0.89 made the calculated equilibrium constants worse (see Table IV)! One interpretation is that the higher energy values of known frequencies are not important in the vibrational partition function, and the polarization functions of the 6-31G** basis do a good job of representing the very low energy "new frequencies." Since there is no known available experimental data for the six new frequencies, this work presents results using these frequencies as found with only small anharmonicity corrections.

The enzymatic assistance of the release of CO_2 from aqueous media[29] has been characterized and is undoubtedly of great interest. However, further studies of the effects of small amounts of H_2O in supercritical CO_2 are needed to characterize the solubilizing mechanism(s) of such a solution in supercritical fluid chromatography.[20] The entropies of association in these equilibria are sensitive to the presence of alternate molecular structures. A trade-off between accuracy in enthalpy and entropy holds while the Gibbs free energy of association appears to be reasonably accurate at the 6-31G** level. The accuracy in K_p follows from the logarithmic dependence on the Gibbs free energy. The present treatment makes use of the ideal gas law for pressures up to about 2 atm. Future work to model supercritical fluid behavior of CO_2 may require the use of an empirical expression for the monomeric gas. Nguyen *et al.*[4] have shown this to give good results for H_2O vapor. Also, it will probably be necessary to include structures of the type $(CO_2)_n(H_2O)$ for the supercritical fluid "phase," but this work shows only one significant cluster of H_2O–CO_2 gives a very good description of the equilibrium compared to data up to 60 atm.

This work has explored the accuracy of an *ab initio* "no-parameter" method and found the "Significant Cluster" model to give very good results in the pressure realm where the ideal gas law is valid. A new "Harmonic-Morse" method of correcting the harmonic frequencies gave improved results compared to either scaled or unscaled harmonic frequencies. The 6-31G** single-determinantal energy calculations provide a near-quantitative treatment of two types of weak interactions, provided the molecular geometries are fully optimized and anharmonic corrections are included within the context of a separate Morse potential fitted to each normal mode.

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APPENDIX

Anharmonicity in water cluster vibrations has recently been treated by numerical solution of the Schrödinger equation along as many as 12 points in each normal coordinate.[30] However, this work employed a simpler method based on only three points fitted by a Morse potential,[31]

$$V = D_e[1 - e^{-a(r-r_e)}]^2. \tag{A1}$$

Here D_e is the depth of the potential minimum calculated by the SCF/HF method for the "Significant Cluster" relative to the energies of the separated atoms in the same basis. In the case of weak interactions, D_e might better be thought of as a partial dissociation of a molecular fragment along a normal coordinate. This is an energy which is less than that of complete dissociation into atoms. Refer to a single-point energy calculation with new coordinates relative to the equilibrium geometry by a displacement along the harmonic normal coordinate of 10%–15% as potential value V in Eq. (1). Then rearrange Eq. (1),

$$1 - \sqrt{\frac{V}{D_e}} = \exp[-a(r-r_e)] \tag{A2}$$

and the parameter a is written in the following form:

$$a = \frac{\ln\left(1 - \sqrt{\frac{V}{D_e}}\right)}{r_e - r}. \tag{A3}$$

Then an effective value of D_e can be obtained if two values of single-point energy V_+ and V_- are known for a ± symmetrical displacement,

$$D_e = \frac{V_+ V_-}{V_+ + 2\sqrt{V_+ V_-} + V_-}. \tag{A4}$$

The *exact eigenvalues* of energy levels with a Morse potential[14] are as follows:

$$E_{\text{Morse}} = hc\omega_e\left(n + \frac{1}{2}\right) - hc\chi_e\omega_e\left(n + \frac{1}{2}\right)^2, \tag{A5}$$

where

$$\chi_e = \frac{hc\omega_e}{4D_e}. \tag{A6}$$

Here χ_e is called the anharmonicity constant. Alternately, if one knows the perturbation parameter b, the energy levels derived from the first-order perturbation theory of a harmonic oscillator[15] by a fourth order displacment are

$$E_{\text{pert}} = h\nu_0\left(n + \frac{1}{2}\right) + \frac{3}{64\pi^4}\ (2n^2 + 2n + 1)\ \frac{h^2 b}{m^2\nu_0^2}. \tag{A7}$$

Equation (A7) can be rewritten as the following two forms, Eq. (A8) and Eq. (A9),

$$E_{\text{pert}} = \left[h\nu_0 + \frac{3h^2 b}{128\pi^4 m^2\nu_0^2\left(n + \frac{1}{2}\right)}\right]\left(n + \frac{1}{2}\right)$$
$$+ \frac{3h^2 b}{32\pi^4 m^2\nu_0^2}\left(n + \frac{1}{2}\right)^2, \tag{A8}$$

$$E_{\text{pert}} = h\nu_0\left(n + \frac{1}{2}\right) + \left[\frac{3h^2 b}{32\pi^4 m^2\nu_0^2}\right.$$
$$\left. + \frac{3h^2 b}{128\pi^4 m^2\nu_0^2\left(n + \frac{1}{2}\right)^2}\right]\left(n + \frac{1}{2}\right)^2. \tag{A9}$$

The "Harmonic-Morse" method constrains the parameter b to be such that the *exact* Morse eigenvalues are met in terms of the harmonic frequency and an "apparent value of D_e." When we set $E_{\text{Morse}} = E_{\text{pert}}$, the coefficients of $(n + \frac{1}{2})^2$ in Eq. (A5) and in Eq. (A9) are equal, and the constant b can be obtained from this relation,

$$b = -\frac{8\pi^4 m^2\nu_0^4}{3D_e}\ \frac{1}{1 + \frac{1}{4\left(n + \frac{1}{2}\right)^2}}. \tag{A10}$$

Also, the coefficients of $(n + \frac{1}{2})$ in Eq. (A5) and in Eq. (A8) are equal,

$$hc\omega_e = h\nu_0 + \frac{3h^2 b}{128\pi^4 m^2\nu_0^2\left(n + \frac{1}{2}\right)}. \tag{A11}$$

Substitute Eq. (A11) and the expression of constant b into Eq. (A5) to obtain

$$E_{Morse} = \left(h\nu_0 + \frac{h^3 \nu_0^3}{32 D_e^2} \frac{4n^2 + 4n + 1}{4n^2 + 4n + 2} \right) \left(n + \frac{1}{2} \right) - \frac{h^2 \nu_0^2}{4 D_e}$$

$$\times \left(n + \frac{1}{2} \right)^2 - \left(\frac{h^2 \nu_0^2}{16 D_e} + \frac{h^4 \nu_0^4}{1024 D_e^3} \right) \frac{4n^2 + 4n + 1}{4n^2 + 4n + 2} \; . \tag{A12}$$

Since the dominant transitions occur from $n = 1 \rightarrow n = 0$, the difference in energy is expressed as follows:

$$E_1 - E_0 = h\nu_0 - \frac{21 h^2 \nu_0^2}{40 D_e} + \frac{h^3 \nu_0^3}{80 D_e^2} - \frac{h^4 \nu_0^4}{2560 D_e^3} \; . \tag{A13}$$

Thus, the vibrational frequency can be computed with Eq. (A13) using an optimized harmonic force field and two additional energy evaluations along the harmonic normal coordinate to determine D_e. The final corrected frequency can then be expressed in terms of the effective well depth and the perturbed harmonic frequency. The only approximation in this numerical procedure is the assumption that the harmonic normal coordinates map directly onto the Morse normal coordinates for small displacements. This work used displacements of 10% and 15%.

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