Chemical Physics
ANNOUNCED Cumulative Examination
Monday, 27 January 2oo3

This examination is concerned with the textbook quantum mechanical example of a harmonic oscillator and the application of the resulting equations to the vibration spectra of small molecules. Some but not all aspects of the examination are cumulative in that later results will use the results of earlier questions.

A. Classical Harmonic Oscillator

Harmonic motion can be modeled by the motion of a mass, m, on a spring anchored to an immovable object. This system follows Hooke's Law, F=-k($\ell - \ell_0$), where "k" is the spring constant and "ℓ" is the displacement from the equilibrium position, "ℓ_0."

(A-1) Write Newton's Equation, F=ma, (a is the acceleration, of course) for the Harmonic
10 Oscillator using the substitution x=$\ell - \ell_0$. Be sure to simplify your result.

(A-2) Show that x(t)=A sin($\omega t + \phi$) is a solution to Newton's Equation. Indicate the
10 meaning of the variables: A, ω, and ϕ. Write an expression for ω in terms of the harmonic oscillator parameters.

(A-3) Use the usual definition of the force in terms of negative derivative of the potential
10 energy to write the potential energy, V(x), for this system. Simplify your result.

(A-4) Write an expression for the total energy of the Harmonic Oscillator, E = KE + V,
10 where KE is the usual form 1/2 mv^2 using your answers to A-2 and A-3. Simplify your result.

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B. Connection to the Morse Potential

The Morse Potential that can be written as: $V(\ell) = D\,(1 - e^{-\beta(\ell-\ell_o)})^2$ as an approximation to the general form of the intermolecular potential energy curve. The Morse Potential for H_2 is shown in the figure below. The fact that the potential has a sharp minimum and is nearly symmetric around the minimum at ℓ_0 is similar to the behavior of the Hooke's Law oscillator potential *in the region near* ℓ_0.

(B-1) Write the Morse Potential in terms of "x," then write the Taylor Series Expansion up to second order of the Morse Potential function around the point x=0, $\ell = \ell_0$, as above. N.B. the simplified result should have only one term in it.

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Recall that a Taylor Series of a function V(x) evaluated at the point "a" is:

$$V(x) \approx V(x=a) + \left(\frac{dV(x)}{dx}\right)_{x=a}(x-a) + \frac{1}{2}\left(\frac{d^2V(x)}{dx^2}\right)_{x=a}(x-a)^2 + \ldots$$

(B-2) Equate your result for the potential energy in B-1 to your result for the Harmonic Oscillator in A-3 and solve for "k" in terms of the Morse Potential parameters.

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(B-3) Find the numerical value of the Force constant "k" in units of Newtons/m for H_2 using the values in the figure below.

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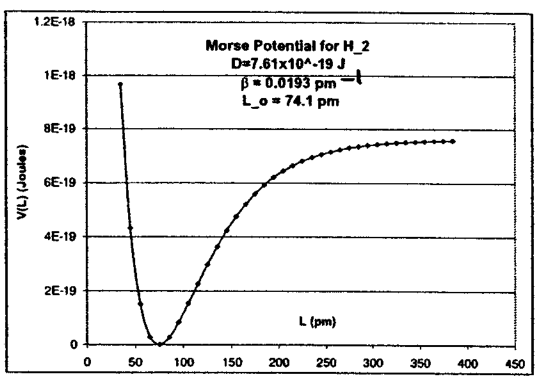

Figure 1: A graph of the Morse Potential for Hydrogen molecules using the parameters: D=7.61x10^{-19} J, β=0.0193 pm^{-1}, and ℓ_0=74.1 pm.

C. **Application to Small Molecules**

In order to extend the simple harmonic oscillator to the vibrational motion of diatomic molecules we also need to replace the single mass attached to a immovable object by an *effective* or *reduced* mass. The reduced mass for a diatomic molecule is simply $\mu = m_1 m_2/(m_1 + m_2)$.

(C-1) Using the formulas from the previous analysis, what is the period of vibrational oscillation of a $^1H_2$ molecule, that is, how long in seconds does it take to undergo one cycle?

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(C-2) Estimate the fundamental vibrational frequency for the isotopically mixed isotope HD or $^2H^1H$.

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(C-3) The $^2H_2$ or deuterium molecule, D_2, has a fundamental frequency of 2990 cm^{-1} but it does not absorb radiation at this frequency, why?

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(C-4) As a very rough estimate assume that the force constant in the $^{12}C^{16}O$ molecule is three times that in H_2. (You should, but need not, be able to justify this assumption.) Make an estimate of the fundamental frequency of this CO molecule. Would you expect $^{12}C^{16}O$ to absorb in the infrared? Why or why not!

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(C-5) What is the most important feature of molecular potentials in general (evident in the Morse Potential as well) that was ignored in the present analysis of vibrational motion? N.B. give a physical explanation not just a one-word answer.

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