

and :

$$(\partial S/\partial x_1)' - (\partial S/\partial x_1)'' \begin{cases} > 0 \rightarrow \text{UCST} , \\ < 0 \rightarrow \text{LCST} . \end{cases} \quad (8)$$

If there is no inflection point in the entropy curve, it follows that the entropy of mixing ΔS_m defined by $\Delta S_m(x_1) \equiv S(x_1) - [x_1 S(1) + (1-x_1)S(0)]$, is positive near an UCST and negative near an LCST.²

To obtain a similar result for the enthalpy H we note that

$$\mu_i' - \mu_i'' = h_i' - h_i'' - T(s_i' - s_i'') = 0 , \quad (9)$$

where h_i and s_i ($i = 1, 2$) denote the partial molar enthalpy and partial molar entropy, respectively. Therefore, we also have

$$(\partial H/\partial x_1)' - (\partial H/\partial x_1)'' \begin{cases} > 0 \rightarrow \text{UCST} , \\ < 0 \rightarrow \text{LCST} . \end{cases} \quad (10)$$

Again it follows that the enthalpy of mixing ΔH_m , defined by $\Delta H_m(x_1) \equiv H(x_1) - [x_1 H(1) + (1-x_1)H(0)]$, is positive near an UCST and negative near an LCST provided the enthalpy curve has no inflection points. Although this cannot be precluded, in general it is rather uncommon. The

derivation shows that these properties are a simple consequence of the stability condition and the assumption of symmetry embodied in Eq. (2) which, although less well satisfied far from the critical point than is the analogous assumption in pure fluids, will be valid extremely close to the critical point.

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On the lowest sigma and pi anion states of Be₂ and Be₃

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The group IIA and IIB metal atoms are known to have low-lying (i. e., slightly unbound) ²P temporary anions,^{1,2} raising the possibility that small clusters of these atoms will possess stable anions resulting from electron addition to low-lying molecular orbitals dominated by the atomic *p* orbitals. Previous calculations^{3,4} have indicated that the ground state anions of Be₂ and Be₃ are bound and are due to the occupation of the *p*_σ rather than the *p*_r orbitals. However, since the basis sets utilized were restricted to *s* and *p* functions and since it has recently been found that correlation effects involving *d* functions are important in the bonding of neutral beryllium and magnesium^{5,7} clusters, we have performed new calculations of the electron affinities (E. A.) of Be₂ and Be₃ using [10s4p/5s2p] (*sp*) and [10s4p1d/5s2p1d] (*spd*) contracted Gaussian basis sets. The *s* and *p* functions are the same as those employed in Ref. 4. The exponent of the *d* function is taken to be 0.20, the value which minimizes the energy of the 1s²2s2p(¹P) state in a configuration interaction calculation.

Self-consistent field (SCF) calculations on the open and closed shell species are performed using the spin-restricted and spin-unrestricted SCF procedures,⁸ respectively. The role of electron correlation is then investigated using second-order many-body perturbation theory (PT). We recognize from the onset that quantitative results are not expected at this level of treatment. Our objective here is to emphasize the *qualitative* changes brought about upon the inclusion of *d* functions in the atomic basis set.

In Fig. 1 we display the SCF and PT potential energy curves of ¹Σ_g⁺Be₂ and the ²Σ_g⁺(1σ_g²1σ_u²2σ_g²2σ_u²3σ_g) and ²Π_u(1σ_g²1σ_u²2σ_g²2σ_u²1π_u) states of Be₂⁻. We first consider the SCF results. With the *sp* basis the minimum in the ²Σ_g⁺Be₂⁻ curve lies energetically below the Be₂ potential curve, while that in the ²Π_u curve lies above the Be₂ curve. The addition of *d* functions stabilizes both anion curves relative to that of the neutral molecule (with a slightly greater effect for the ²Π_u curve) giving rise to small (~0.05 eV) increases in the E. A.'s.

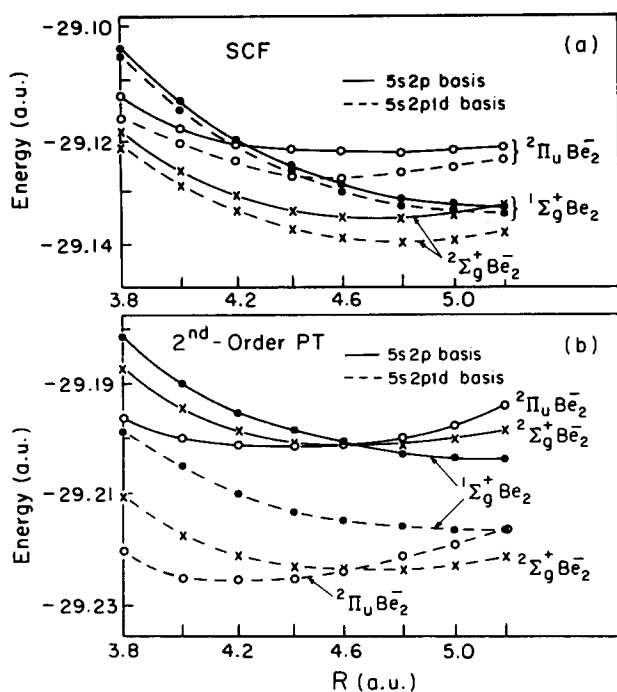


FIG. 1. Potential energy curves of Be₂ and Be₂⁻: (a) SCF curves, (b) second-order PT curves. Solid lines denote results obtained using the 5s2p basis set and the dashed lines the results of the 5s2p1d basis set. The 1Σ_g⁺Be₂ and 2Σ_g⁺ and 2Π_uBe₂⁻ curves are denoted by dots, x's, and open circles, respectively.

Correlation effects stabilize in the 2Π_u anion more than the 2Σ_g⁺ anion, leading to a crossing between the two curves near a bond length of 4.6 a.u. The *spd* PT calculations indicate that the 2Π_u anion has a bond length of about 4.22 a.u. and a vertical detachment energy of 0.84 eV while the 2Σ_g⁺ anion has a bond length of about 4.62 a.u. and a detachment energy of 0.30 eV.⁹

The situation for linear Be₃ is similar to that for Be₂: At the SCF level of treatment the 2Σ_u⁺ anion is more stable than the 2Π_u anion. The inclusion of correlation in the *spd* basis increases the pi E.A. by 0.50 eV and decreases the sigma E.A. by 0.28 eV, causing the 2Π anion to be the more stable species. The PT calculations yield vertical detachment energies of 0.70 eV (*R* = 4.6 a.u.) and 0.95 eV (*R* = 4.2 a.u.) for the 2Σ_u⁺ and 2Π_u states, respectively. We expect that these results will carry over to the equilateral form of Be₃, and that correlation effects will cause the 2A'' (pi) anion to be more stable than the 2A' (sigma) anion, in contrast to the SCF predictions.

The destabilization of the 2Σ_u⁺ anion of Be₃ relative to the neutral upon the inclusion of correlation effects contradicts the common notion that correlation in anions should exceed that in their neutral parents. However, there is a simple explanation for this seeming contradiction: the formation of the 2Σ_u⁺ anion by addition of an electron to the 3σ_u orbital removes the possibility for the 4σ_g² - 3σ_u² excitation, which plays an important role in correlating the neutral species. Although this

excitation is blocked in the 2Σ_u⁺ anion, it is still "open" in 2Π_uBe₃⁻, resulting in a greater importance of correlation for the latter. A similar "blocking" of the 2σ_u² - 3σ_g² excitation apparently destabilizes the 2Σ_g⁺Be₂⁻ ion, especially for the *sp* basis set.

Previously we reported that an SCF level of treatment also gives rise to stable quartet states of Be₃⁻. In second-order PT (using the *spd* basis) the 4Π_g(1σ_g²1σ_u²2σ_g²2σ_u3σ_g1π_u) and 4Δ_u(1σ_g²1σ_u²2σ_g²2σ_u1π_u²) quartet states of linear Be₃ have electron detachment energies of 0.63 and 1.4 eV, respectively. These values are about 0.7 eV less than the corresponding SCF values but are still surprisingly large, perhaps indicating the inadequacy of second-order PT for the quartet states.

Whereas our previous studies indicated that the ground state anions of Be₂ and Be₃ are sigma species, the present results suggest that the doublet sigma and pi anions have nearly the same energy, with the pi anions being slightly more stable.^{10,11} Due to the toxicity of beryllium, experimental results are more likely to be forthcoming for the magnesium compounds. However, one should be cautious in extrapolating the present results to the corresponding magnesium species since recent theoretical studies have indicated rather different bonding mechanisms in the beryllium and magnesium clusters.⁷

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⁹The results for Be₂ were checked at *R* = 4.22 and 4.62 a.u. using third-order PT. No significant changes were introduced into the relative energies of the two anion states and the ground state neutral with this refinement.

¹⁰Although the 2Π_u and 2Σ_g⁺ curves of Be₂⁻ are bound in the sense that at their minima they lie below the neutral curve, their energies at the minima are only slightly below that of 2Be. If the *ν* = 0 levels of the anions fall above the 2Be asymptote,

the anions will be metastable since electron detachment can occur. Although the present calculations are not sufficiently quantitative to allow us to make a definitive statement about the metastability, we can conclude that even if the anions are metastable, they will have long lifetimes in their $\nu=0$ states since the Franck-Condon overlap between the anion vibration-

al wave functions and those of Be_2 will be small.

¹¹Here we assume that the ground state anions have doublet multiplicities. A more thorough treatment of correlation is actually required to determine whether the ground state of Be_2^- is a doublet or a quartet. Such calculations are presently underway.

Franck-Condon factors with vibration-rotation interaction for Morse oscillators

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Accurate knowledge of Franck-Condon factors (FCfs) of diatomic molecules is of fundamental importance for diagnosis of physical conditions existing in astronomical and aeronautical light sources, for studies of molecular structure, and for chemical studies involving reactions between atoms and molecules. A Gauss-Laguerre quadrature method (GLQM) was introduced by the authors¹ using Morse oscillators² for the calculation of these FCfs. This method was applied to the calculation of FCfs for the $B-X$ system of the BH molecule and the results were in excellent agreement with those evaluated by Jarman's³ procedure. This method is simple and valid for all vibrational quantum numbers for which the Morse potential is valid. The purpose of this article is to show how the GLQM can be used to derive the FCfs, including vibration-rotation interaction. Molecular rotation effects the vibration through the centrifugal part of the potential, and thus the vibrational wave functions depend on the rotational quantum number J . The effect of vibration-rotation interaction on FCfs, usually assumed to be negligible for relatively low J values,⁴ is expected to play a significant role,⁵ especially for molecules having low reduced mass such as alkali hydrides.

Band intensity measurements are frequently used for thermometric purposes in flames and shock tube sources, where appreciable number of diatomic molecules are found in relatively higher rotational levels. Hence, the neglect of vibration-rotation interaction leads to the derivation of erroneous conclusions. Therefore, it is felt worthwhile to extend the GLQM to include vibration-rotation interaction. We have chosen to study the $A-X$ system of hydroxyl radical.

For this purpose, the Morse-Pekeris model⁶ with the slight modification given by Shumaker⁷ has been used. In this model, the radial wave function for the Morse potential

$$U(r) = D_e \{1 - \exp[-\alpha(r - r_e)]\}^2 + \frac{J(J+1)}{2\mu r^2} \dots \quad (1)$$

is given by

$$\psi_{vJ} = N_{vJ} \exp(-\frac{1}{2}Z) Z^{b/2} L_{v,b}^b(Z) \dots, \quad (2)$$

where

$$\begin{aligned} Z &= K_1 \exp[-a(r - r_0)], \\ r_0 &= r_e(1 + \alpha), \\ b &= K_2 - 2v - 1, \\ K_1 &= 2[(D_2 + C_2)/\omega_e X_e]^{1/2}, \\ K_2 &= [2(2D_1 - C_1)\omega_e X_e K_1], \\ D_1 &= D \exp(-ar_e\alpha), \\ D_2 &= D \exp(-2ar_e\alpha), \\ C_1 &= [A/r_0 a(1 + \alpha)^2] [4 - (6/ar_0)], \\ C_2 &= [A/ar_0(1 + \alpha)^2] [(3/ar_0) - 1], \\ \alpha &= 4AB_e/\omega_e^2, \\ A &= B_e J(J+1). \end{aligned}$$

TABLE I. Franck-Condon factors for the $A-X$ system of OH.

v', v''	J	$q_{v',v''}^{J,J'}$		
		Present work	Ref. 11	Ref. 12
0, 0	1	0.908		0.914
	1.5	0.908	0.907	
	5	0.906		0.911
	10	0.900		0.904
	15	0.890		0.892
	20	0.874		0.874
	25	0.850		0.849
2, 2	25.5	0.847	0.843	
	1.5	0.523	0.507	
	25.5	0.268	0.281	