Potential Energy Surfaces for Alkali-Trimers

S. Noor Mohammad

Department of Chemistry, Indian Institute of Technology, Kharagpur-721302, India

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Semi-empirical potential energy surfaces for alkali-trimers are derived from the simplest form of London's approximation, by evaluating the Coulomb and exchange integrals as half of the sum and difference of two new interaction potential curves for the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of the corresponding alkali dimers. The trimers attain maximum stability in their linear symmetric configuration. The force constants corresponding to stretching and bending deformations of the homonuclear trimers have been calculated for the linear symmetric configuration. Unlike the stretching, the bending deformation is seen to be very much insensitive to the ground state energy variation of the trimers.

An accurate knowledge of potential energy surfaces is of considerable importance in the study of reaction cross-sections and isotope effects in exchange reactions. In the present communication we report the results of investigations on such surfaces for alkali-trimers based on London's formula [1]. Only the ns valence electron of each alkali atom is explicitly taken into account. All the trimers are thus reduced to three-electron three-orbital systems.

The potential surface is of the form

$$E_{\pm} = Q_{ab} + Q_{bc} + Q_{ca} \pm 2^{-1/2} [(J_{ab} - J_{bc})^2 + (J_{bc} - J_{ca})^2 + (J_{ca} - J_{ab})^2]^{1/2} \quad (1)$$

where

$$Q = 0.5\,(E_s + E_t) \quad \text{and} \quad J = 0.5\,(E_s - E_t)\,. \quad (2)$$

E_s and E_t are diatomic singlet and triplet potential curves.

For the diatomic singlet curve we use the recently proposed function [2]

$$E_s = D_e (y^2 - 2y) \quad (3)$$

where

$$y = (r_e/r)^n \exp\{-b(r^m - r_e^m)\}\,,$$
$$b = (w-n)/m\, r_e^m\,,$$
$$m = 2 + (w-4)(w-2)/4(w-1)\,,$$
$$w = (k_e r_e^2/2 D_e)^{1/2}\,, \quad (4)$$

and $n = 1.0$ for $w \lesssim 3.2$,
$= 0.6$ for $w \gtrsim 3.2$.

D_e is the dissociation energy, r_e the equilibrium internuclear distance and k_e the force constant.

Reprint requests to Dr. S. Noor Mohammad, Department of Physics and Meteorology, Indian Institute of Technology, Kharagpur 721302, W. B., India.

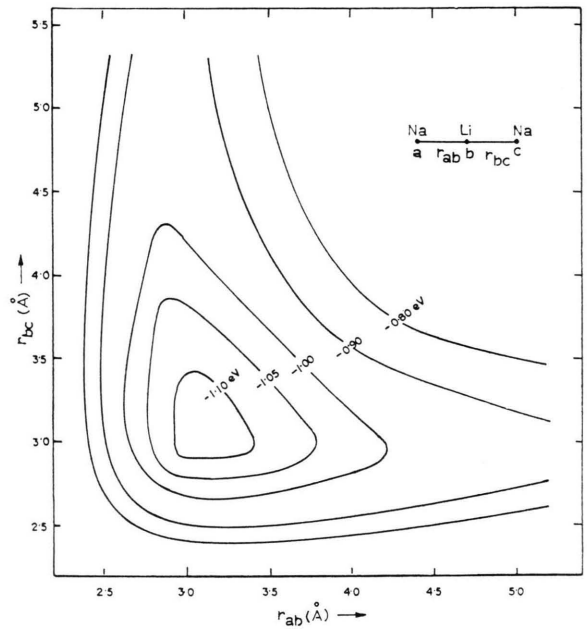

Fig. 1. Potential energy surfaces of NaLiNa for linear configuration.

We devise the triplet curve as $E_t = 0.5\,(y^2 + 0.05\,y)$. This curve is obtained by fitting to the ab initio data [3–5] of Li_2, LiNa and Na_2. Since alkali-trimers behave quite ideally with respect to semi-empirical parametrization, we believe that E_t will represent equally well the rest of the diatomics of the series.

The potential parameters D_e, r_e and k_e needed to define E_s and E_t were taken from Herzberg [6], Hessel [7], and from the summary of Evans et al [8]. The binding energy E_- of alkali-trimers was then calculated from Eq. (1) for a large number of linear and bent configurations. The potential energy surface for the linear configuration of NaLiNa is shown

Table 1. Calculated values[a] of binding energy (Δ) and bond lengths (r_{ab}, r_{bc}) of alkali-trimers in collinear and isosceles triangular configurations.

A+B$_2$	→ ABB (BAB) / → AB+B	$-\Delta$ (kcal/mole) Δ_r	Δ_p	r_{ab} (Å)	r_{bc} (Å)
Li+Li$_2$	→ LiLiLi	6.69	6.69	2.87	2.87
	→ Li$_2$+Li	4.48	4.48	3.74	2.672
Na+Na$_2$	→ NaNaNa	4.61	4.61	3.30	3.30
	→ NaNaNa	4.61	4.61	3.20	3.20
K+K$_2$	→ KKK	3.34	3.34	4.10	4.10
	→ K$_2$+K	2.26	2.26	5.15	3.923
Rb+Rb$_2$	→ RbRbRb	3.13	3.13	4.31	4.31
	→ Rb$_2$+Rb	2.11	2.11	5.45	4.127
Cs+Cs$_2$	→ CsCsCs	2.85	2.85	4.70	4.70
	→ Cs$_2$+Cs	1.95	1.95	5.80	4.465
Li+Na$_2$	→ LiNaNa	7.06	3.83	3.00	3.42
	→ LiNa+Na	3.75	0.53	4.06	3.08
Li+Na$_2$	→ NaLiNa	8.86	5.63	3.12	3.12
	→ NaLi+Na	—	—	—	—
Na+Li$_2$	→ NaLiLi	4.50	8.42	3.20	2.82
	→ NaLi+Li	3.77	7.69	3.95	2.672
Na+Li$_2$	→ LiNaLi	1.66	5.58	3.10	3.10
	→ LiNa+Li	—	—	—	—
K+Li$_2$	→ KLiLi	3.14	10.31	3.58	2.673
	→ KLi+Li	3.21	10.30	4.26	2.673
K+Li$_2$	→ LiKLi	—	4.68	3.40	3.40
	→ LiK+Li	—	—	—	—
K+Na$_2$	→ KNaNa	3.07	6.07	3.80	3.17
	→ KNa+Na	2.63	5.63	4.45	3.08
K+Na$_2$	→ NaKNa	0.88	3.87	3.74	3.74
	→ NaK+Na	—	—	—	—
Na+K$_2$	→NaKK	4.75	2.68	3.68	4.30
	→ NaK+K	2.65	0.58	4.78	3.923
Na+K$_2$	→ KNaK	0.26	3.87	3.71	3.71
	→ KNa+K	—	—	—	—
Li+K$_2$	→ LiKK	7.29	2.24	3.27	4.47
	→ LiK+K	0.14	—	4.60	3.923
Li+K$_2$	→ KLiK	9.75	4.67	3.41	3.41
	→ KLi+K	—	—	—	—
Rb+Na$_2$	→ RbNaNa	2.63	6.55	3.84	3.20
	→RbNa+Na	2.42	6.34	4.50	3.08
Rb+Na$_2$	→ NaRbNa	—	3.57	3.77	3.77
	→ NaRb+Na	—	—	—	—
Na+Rb$_2$	→ NaRbRb	4.36	2.58	3.82	4.40
	→ NaRb+Rb	2.44	0.67	4.90	4.127
Na+Rb$_2$	→ RbNaRb	5.40	3.62	3.81	3.81
	→ RbNa+Rb	—	—	—	—

[a] The upper and lower results in each row correspond to collinear and isosceles triangular configurations respectively; Δ_r is the binding energy with respect to reactant, Δ_p is the binding energy with respect to product.

Table 2. Calculated force constants (mdyne/Å) for the ground state of homonuclear alkali-trimers.

Trimer	k_{11} (symmetric stretching)	$k_{22}\times 10$ (asymmetric stretching)	$k_{33}\times 10^5$ (bending)
Li$_3$	0.1213	0.3972	11.595
Na$_3$	0.1071	0.2587	4.963
K$_3$	0.0541	0.1444	0.939
Rb$_3$	0.0454	0.1179	0.830
Cs$_3$	0.0347	0.1008	0.518

in Figure 1. The potential energy surfaces of other trimers are quite similar to that of NaLiNa. All these surfaces exhibit a shallow potential well at small internuclear distances and extend into the entrance and exit valleys without an energy barrier. The depths of these wells represent the binding energies of trimers, which in the case of symmetric ones decrease in the order $Li_3 > Na_3 > K_3 > Rb_3 > Cs_3$ in consonance with the bond energy values of the corresponding dimers. However, in the mixed alkali cases the potential well is deepest when the lighter alkali occupies the central position. Calculated values of binding energies and bond lengths of the trimers are given in Table 1. It can be seen from this table that symmetric trimers attain greatest stability in the linear symmetric configuration. In all cases the bond length of a trimer is greater than the bond length of the corresponding dimer.

Since the stablest configuration is linear and symmetric, it can be characterized by the force constants of its stretching and bending deformations. Using the procedure of Micha et al.[9] we have calculated these force constants for only the homonuclear trimers. These are given in Table 2. Very low values of the bending force constants indicate that the energy of the ground state is quite insensitive to small changes in interbond angle.

No experimental values are yet available for any of the quantities calculated in the present investigation. Whitehead and Grice[10], however, made a similar type of calculations using ab initio[3–5] and RKR[11,12] curves for Li_2, LiNa and Na_2. The present results are seen to be in good agreement with them.

The most distinguishing feature of the present method is that with only the knowledge of D_e, r_e and k_e one can obtain a reasonable description of potential surfaces of alkali-trimers.

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