1062 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (4), 1062—1067 (1978) [Vol. 51, No. 4

The Interaction Potential Surfaces for Alkali-trimers

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(Received August 27, 1977)

Semi-empirical potential energy surfaces for some alkali-trimer complexes have been calculated using the simplest form of London equation. In the calculations use has been made of two new exponential potentials for the singlet and triplet states of diatomic molecules. The calculated potential surfaces at small internuclear distances show shallow well extending into the entrance and exit valleys without an energy barrier. The complexes are seen to be stable over all configurations; they are most stable however in the linear symmetric configuration. The force constants corresponding to bending and stretching deformations have been calculated for homonuclear trimers only. It has been observed that unlike stretching, the bending deformations do not sensitively affect the energy variation of the ground state.

The alkali atom-alkali dimer exchange reaction

$$L' + L_2 \longrightarrow L'L + L, \quad (1)$$

where L and L′ are same or different atoms, are believed to be important in determining the energy transfer and condensation in supersonic alkali nozzle beams(1) and in determining nuclear relaxation times observed in the NMR of alkali dimers in optically bumped alkali vapours.(2) Recently some molecular beam reaction scattering has been measured(3) for $Na+Cs_2$, Rb_2, K_2, and $K+Rb_2$. A knowledge of potential energy surfaces of the trimer complexes formed therein is of considerable importance in order to help resolve the reaction dynamics, to determine the reaction cross-section and isotope effects, and to provide theoretical interpretation of the reactive scattering data.

Alkali trimers are intermediate of alkali atom-dimer exchange reaction. The experimental observation of Foster *et al.*(4) indicates only that they are stable molecules and suggests nothing about their binding energy and geometry. A diatomics-in-molecules calculation(5) for Li_3 shows it to be a stable molecule bound approximately by 9 kcal/mol with respect to $Li+Li_2$. The recent *ab initio* calculation(6) of Davies *et al.*, on the other hand, suggests that linear Li_3 is bound 3 kcal/mol lower in energy with respect to the same reactants. Pseudopotential calculations(7) on Na_3 and K_3 indicate that they are unbound with respect to atom-dimer dissociation. Semi-empirical valence bond calculations,(8) however, show that linear trimers are stable molecules in the ground state.

In the present study our aim is to determine semi-empirically the potential energy surfaces of some alkali trimer complexes and to obtain thereform their binding energies, equilibrium geometries and equilibrium vibrational force constants.

Method of Calculation

A non-ionic valence bond method has been used in the present calculation. Only the ns valence electron of each alkali atom is explicitly taken into consideration. All the trimers are thus reduced to three-electron three-orbital systems. The Hamiltonian operator for such systems in atomic units is

$$H = \sum_{i}[-\nabla_i^2/2 - \sum_{a} Z_a/r_{ai} + \sum_{i>j} 1/r_{ij}] + \sum_{a>b} Z_a Z_b/R_{ab}, \quad (2)$$

where the subscripts i, j, *etc.* refer to electrons and a, b, *etc.* to nuclei. There are two linearly independent canonical structures ϕ_1 and ϕ_2 coresponding to the bonding scheme (a—b,c) and (a,b—c) respectively. If one assumes that the orbitals a,b, and c are mutually orthogonal, the secular determinant written in terms of the Hamiltonian matrix elements H_{ij} and the overlap matrix elements S_{ij} will yield

$$E_\pm = Q_{ab} + Q_{bc} + Q_{ca} \pm 2^{-1/2}[(J_{ab}-J_{bc})^2 + (J_{bc}-J_{ca})^2 + (J_{ca}-J_{ab})^2]^{1/2}. \quad (3)$$

Here Q and J are the diatomic Coulomb and exchange integrals respectively. These integrals have been evaluated at the three internuclear distances R_{ab}, R_{bc}, and R_{ca}. This equation is known as London equation.(9) In Eq. 3 the zero of the energy refers to the separated atoms and since Q and J are both negative quantities E_- refers to the binding energy of more stable state. However, the diatomic integrals Q and J are more difficult to evaluate for alkali diatomics. In order to circumvent this difficulty, we adopt the semi-empirical method of Cashion and Herschbach,(10) and obtain from identical valence bond approximation

$$E_\pm = Q \pm J, \quad (4)$$

where E_+ and E_- refer to $^1\Sigma_g$ and $^3\Sigma_u$ states respectively. If these potential curves are known independently Q and J can be evaluated as

$$Q = \frac{1}{2}[E(^1\Sigma)+E(^3\Sigma)], \quad (5)$$

and

$$J = \frac{1}{2}[E(^1\Sigma)-E(^3\Sigma)]. \quad (6)$$

The problem thus reduces to obtaining accurate potential energy curves for the $^1\Sigma_g$ and $^3\Sigma_u$ electronic states of alkali diatomics.

Diatomic Potential Curves

Singlet Potential. Whitehead and Grice,(8) in their studies of atom-dimer exchange reaction of lithium and sodium, made use of *ab initio*(11—15) and RKR(16) curves for Li_2, LiNa, and Na_2. Due to lack of similar data on the other dimers of alkali atoms, it is not possible to extend their method to the trimers involving atoms other than Li and Na. Recently the classical turning points for the vibrational levels of the $^1\Sigma_g$ state of K_2, Rb_2, and Cs_2 have also been derived.[17] One major disadvantage of these curves is that these are constructed only in the region for which sufficient spectroscopic data exist. For Li_2, data for the higher vibrational levels being not available, Krupenie *et al.*[16] fitted its RKR curve to the Lippincott potential[18–21] to get extrapolation at large internuclear distances. Another disadvantage of this method is that it gives only numerical values of the curve at a series of points, and not a suitable analytical form for the same. Further, these curves are not available for the heteronuclear diatomics of the present series. Recently Sannigrahi *et al.*[22] have used Morse[23] and Rydberg[24] potentials for the $^1\Sigma_g$ state. But in case of alkali dimers it can be seen[25] that the Morse potential predicts too much attraction at large internuclear distances. Though the Rydberg potential is much better than the Morse, in many cases it deviates greatly from the RKR curves, and on the average, predicts α_e within -3.2% and $\omega_e x_e$ within 11.74% for the fifty diatomic molecules studied.[26] In our recent study[26] of the interatomic potentials for the bound states of diatomic molecules we have proposed a new potential,

$$U_2(R) = D_e\left\{\left(\frac{R_e}{R}\right)^{2n}\exp\left[-2\alpha(R^2-R_e^2)\right] -2\left(\frac{R_e}{R}\right)^{n}\exp\left[-\alpha(R^2-R_e^2)\right]\right\}, \tag{7}$$

where

$$\alpha = (\Delta^{1/2}-n)/2R_e^2, \tag{8}$$

$$\begin{aligned} n &= 0.324 + 0.313\Delta^{1/2} + 0.01\Delta \quad \text{for } 0 \lesssim \Delta^{1/2} \lesssim 3.2 \\ &= 1.3637 - 0.206\Delta^{1/2} + 0.004\Delta \quad \text{for } 3.2 \lesssim \Delta^{1/2} < \infty, \end{aligned} \tag{9}$$

and

$$\Delta = R_e^2 k_e/2D_e.$$

$-D_e$ is the minimum value of $U_2(R)$, R_e is the value of R at which $U_2(R) = -D_e$ and k_e is the measure of curvature of the potential curve at $R=R_e$. A detailed investigation shows that this is perhaps the best three-parameter potential over an extended region of R. It predicts α_e and $\omega_e x_e$ and other spectroscopic constants such as higher order vibrational force constants n_e and o_e almost exactly for a large number of molecules. This is, in fact, a generalisation of the Vershni III potential.[27] In Fig. 1 we have compared this potential with the corresponding Varshni III, RKR and *ab initio* curves for Li_2, LiNa, and Na_2. The curves of this figure shows that the present potential is equally applicable to the other alkali dimers also. We use this potential for the $^1\Sigma$ ground state.

Triplet Potential. Except for a long range van der Waals attraction the $^3\Sigma_u^+$ excited electronic state is a repulsive one and no experimental information is available for this. We are, therefore, to depend for this on a reliable theoretical calculation. Since the interaction of two alkali metal atoms is qualitatively similar to the interaction of two hydrogen atoms whose theoretical curve can be accurately constructed by the perturbation method of Dalgarno and Lynn,[28] Davies *et al.*[6] in their calculations of collision integrals, used the same to predict the triplet curves for alkali metal diatomics. These are given by 60.70 $\exp(-1.37\,R)$, 105 $\exp(-1.51\,R)$, 211 $\exp(-1.45\,R)$, 170 $\exp(-1.34\,R)$, and 173 $\exp(-1.27\,R)$ for Li_2, Na_2, K_2, Rb_2, and Cs_2 respectively. The main defect of this method is that it gives an individual potential for each dimer. Krupenie *et al.* used a method originally suggested by Keyes[29] to estimate the $^3\Sigma_u^+$ potential of Li_2. He simply changed the sign in the exchange term of the double exponential function representing the $^1\Sigma_g^+$ potential. When compared with the *ab initio* curve, this is seen to lie too high by a factor of 2 to 4.

In connection with some classical trajectory studies of alkali atom-dimer exchange reactions Whitehead[30] has recently proposed a Porter-Karplus[31] type anti-Morse potential for Li_2, LiNa, and Na_2. This is given by

$$U_w^{(3)}(R) = D_e^{(3)}[(x+1)^2-1], \tag{10}$$

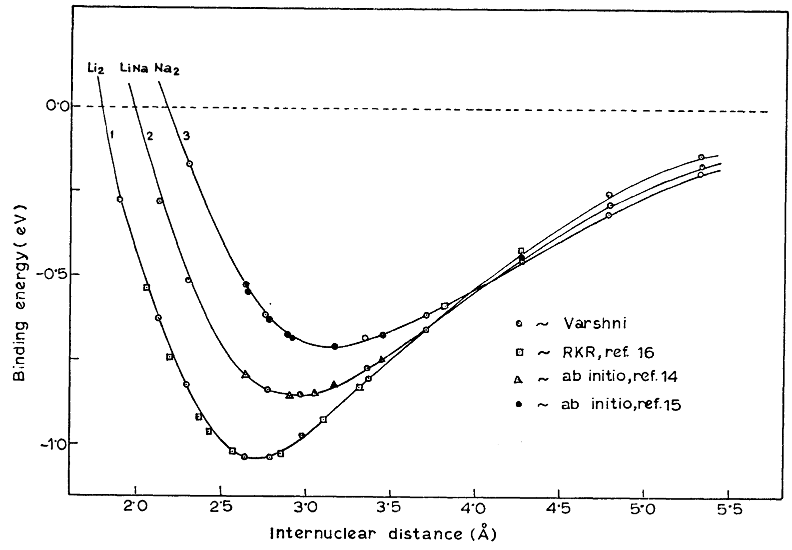

Fig. 1. Comparison of potential energy curves for the ground state of Li_2, LiNa, and Na_2.

where

$$x = \exp\left[-\beta^{(3)}(R-R_e)\right]. \tag{11}$$

$D_e^{(3)}=3.30$, 3.09, and 3.30 kcal/mol and $\beta^{(3)}=1.240$, 1.254, and 1.230 Å^{-1} for Li_2, LiNa, and Na_2 respectively. Equation 10 has been obtained by fitting to the *ab initio* data. The main objection to $U_w^{(3)}(R)$ is that it requires an independent knowledge of the triplet state potential data which uptill now are available only for Li_2, LiNa and Na_2. Consequently its applicability is limited to these dimers only.

With a view to devising a triplet potential of general validity we change the sign of the repulsive part of Eq. 7 and then fit it to the *ab initio* data[12–15] to get

$$U_2^{(3)}(R) = 0.50D_e\left\{\left(\frac{R_e}{R}\right)^{2n}\exp\left[-2\alpha(R^2-R_e^2)\right] + 0.05\left(\frac{R_e}{R}\right)^{n}\exp\left[-\alpha(R^2-R_e^2)\right]\right\}. \tag{12}$$

Like its singlet counterpart it is expected to show correct limiting behaviour at large internuclear distances. We tried to construct the triplet potential corresponding to the Varshni also and it is interesting to see that it comes out as the same as Eq. 12 with $n=1$. The identifying feature of these potentials is that they can be expressed in terms of the ground state potential parameters for which sufficient informations are available for the present systems. In Fig. 2 we have compared Eq. 12 with the corresponding Varshni (triplet) and *ab initio* curves for Li_2, LiNa and Na_2. It can be seen from this figure that the said potential agrees quite well with the latter curves. Since alkali dimers behave quite ideally with respect to semi-empirical parametrisation, we believe that this potential (which has been obtained only for the specific cases of Li_2, LiNa and Na_2) might also be useful for the rest of the diatomics in the series. We use this potential for the triplet state.

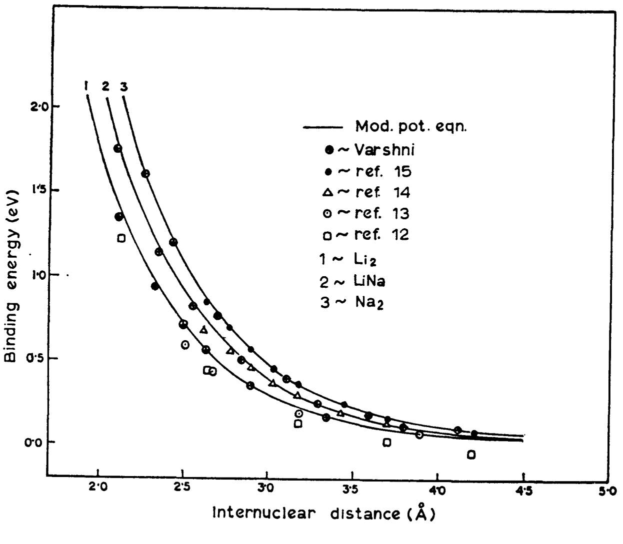

Fig. 2. Comparison of potential energy curves for the triplet state of Li_2, LiNa, and Na_2.

Results

The potential parameters D_e, R_e, and K_e needed to evaluate Eqs. 7 to 12 are given in Table 1. All these data are taken from Herzberg[32)] and from the summary of Evans *et al.*[33)] Using Eq. 3 potential energy surfaces consisting of a series of contour lines of constant energy are now constructed for all the triatomic complexes for both Varshni III and our own potential model. Such surfaces for the linear configuration of Li_3, LiLiNa and, NaLiNa are shown in Figs. 3 to 5. Potential energy surfaces of other trimers, which are not shown in the figure are similar to those of Li_3, LiLiNa, and NaLiNa. These surfaces are very much important in the sense that can provide useful informations towards detailed rate calculation by the solution of classical equation of motion. All these surfaces exhibit shallow potential well at small internuclear distances which extends into the entrance and exit valleys without an energy barrier.

TABLE 1. GROUND STATE POTENTIAL PARAMETERS FOR ALKALI-DIMERS

Dimer	$-D_e$(eV)[e)]	r_e(Å)[e)]	k_e(mdyn/Å)[e)]
Li_2	1.05	2.672	0.256
Na_2	0.74	3.08	0.174
K_2	0.52	3.923	0.099
Rb_2	0.493[a)]	4.127[a)]	0.081
Cs_2	0.453[a)]	4.465[a)]	0.069
LiNa	0.88[c)]	2.911[b)]	0.195[d)]
LiK	0.739[c)]	3.238[c)]	0.149
NaK	0.61	3.476[c)]	0.129
NaRb	0.57	3.565	0.122

a) Taken from Ref. 33. b) Taken from Ref. 14. c) Determined by the formula $x_{ab}=(x_{aa}\,x_{bb})^{1/2}$, where all x_{aa} are taken from Refs. 32 and 33. d) Calculated from the observed vibrational frequency, see Ref. 32. e) All these data except those taken from a, b, c, and d are from Ref. 32. The vibrational force constants are calculated from the observed vibrational frequency given in this reference.

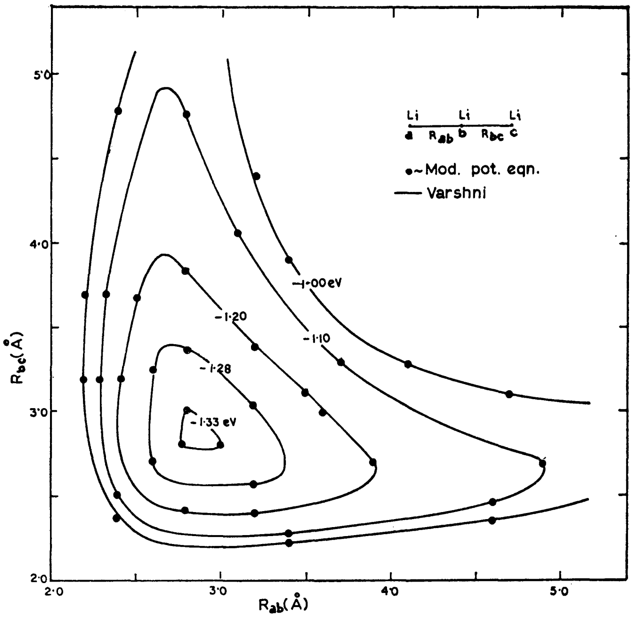

Fig. 3. Potential energy surfaces of Li_3 for linear configuration.

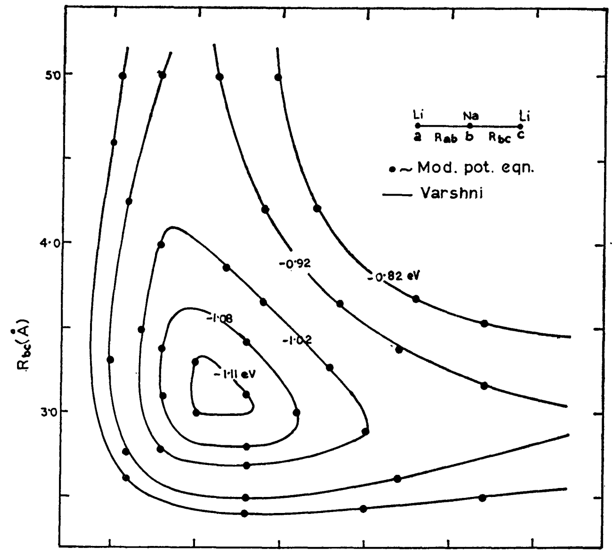

Fig. 4. Potential energy surfaces of LiNaLi for linear configuration.

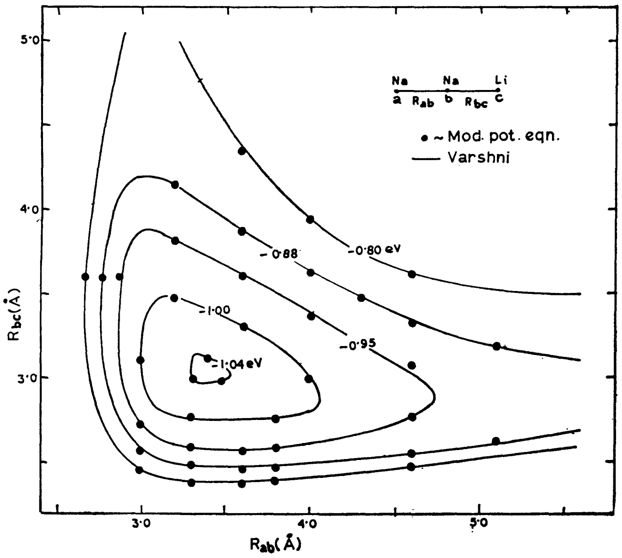

Fig. 5. Potential energy surfaces of NaNaLi for linear configuration.

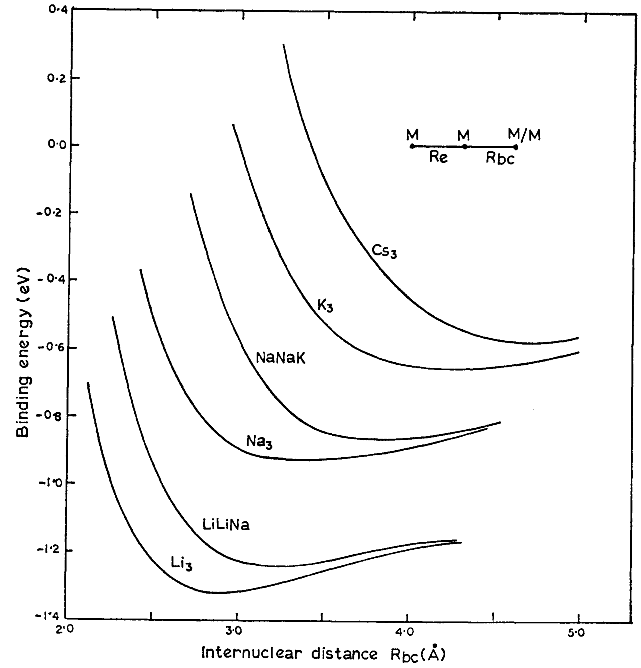

Fig. 6. Energy curves for approach of M (or M′) to M_2 fixed at M_2 equilibrium internuclear distances in the linear configuration for Li_3, LiLiNa, Na_3, NaNaK, K_3, and Cs_3.

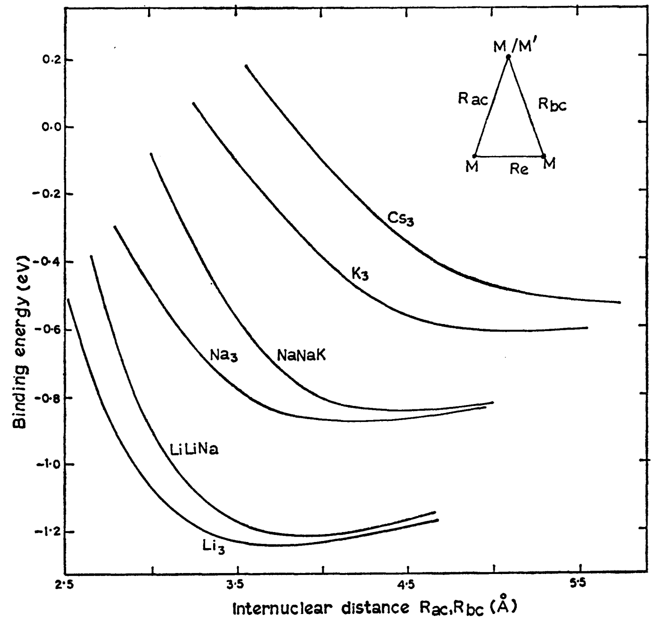

Fig. 7. Energy curves for approach of M (or M′) to M_2 fixed at M_2 equilibrium internuclear distances in the isosceles triangular configuration for Li_3, LiLiNa, Na_3, NaNaK, K_3, and Cs_3.

The reacting atom, coming along the entrance valley is first reflected back and forth at the sides of the basin and undergoes a continual conversion of translational into vibrational energy and vice versa. As a result, the atom wanders about the potential basin until it either passes out through the gap into the exit valley which means reaction has taken place or it returns to the valley whence it entered. The depths of the potential wells are defined to be the binding energy of trimers. These binding energies in the case of symmetric trimers are found to decrease in the order $Li_3 > Na_3 > K_3 > Rb_3 > Cs_3$ in line 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. The variation of binding energy of Li_3, Na_3, LiLiNa, NaNaK, K_3, and Cs_3 with bond length are shown in Figs. 6 and 7 for collinear and isosceles triangular configurations respectively. In each case the reacting alkali dimer is kept fixed at its equilibrium internuclear distance R_e, and binding energy is plotted as a function of the reactant alkali distance. Calculated values of binding energy and bond length are given in Table 2. It can be seen from this table that the symmetric alkali trimers are most stable in the linear symmetric configuration. The bond length of a trimer is in general greater than the bond length of the corresponding dimer.

TABLE 2. CALCULATED VALUES OF BINDING ENERGIES ($\mathit{\Delta}$) AND BOND LENGTHS (r_{ab}, r_{bc}) FOR ALKALI TRIMERS IN LINEAR SYMMETRIC AND ISOSCELES TRIANGULAR CONFIGURATIONS

$M'+M_2$ $\rightarrow(M'MM)$ $\rightarrow M'M+M$	$-\mathit{\Delta}$ (kcal/mol)[a)] $\mathit{\Delta}_r$	 $\mathit{\Delta}_p$	r_{ab}(Å)	r_{bc}(Å)
$Li+Li_2$ $\rightarrow$(LiLiLi) $\rightarrow Li_2+Li$	6.58 4.50	6.58 4.50	2.85 3.68	2.85 2.67
$Na+Na_2$ $\rightarrow$NaNaNa $\rightarrow Na_2+Na$	4.70 3.18	4.70 3.18	3.27 4.21	3.27 3.08
$K+K_2$ $\rightarrow$KKK $\rightarrow K_2+K$	3.46 2.24	3.46 2.24	4.05 5.08	4.05 3.923
$Rb+Rb_2$ $\rightarrow$RbRbRb $\rightarrow Rb_2+Rb$	3.23 2.12	3.23 2.12	4.28 5.50	4.28 4.127
$Cs+Cs_2$ $\rightarrow$CsCsCs $\rightarrow Cs_2+Cs$	2.93 1.96	2.93 1.96	4.68 5.83	4.68 4.465
$Na+Li_2$ $\rightarrow$NaLiLi $\rightarrow$NaLi+Li	4.61 3.81	8.53 7.72	3.30 3.89	2.80 2.672
$Na+Li_2$ $\rightarrow$LiNaLi $\rightarrow$LiNa+Li	1.73 —	5.65 —	3.12 —	3.12 —
$Li+Na_2$ $\rightarrow$LiNaNa $\rightarrow$LiNa+Na	7.03 3.75	3.81 0.52	2.97 4.10	3.40 3.08
$Li+Na_2$ $\rightarrow$NaLiNa $\rightarrow$NaLi+Na	8.88 —	5.65 —	3.15 —	3.15 —
K+Li $\rightarrow$KLiLi $\rightarrow$KLi+Li	3.16 3.16	10.33 10.33	3.60 4.20	2.68 2.672
$K+Li_2$ $\rightarrow$LiKLi $\rightarrow$LiK+Li	— —	4.68 —	3.44 —	3.44 —
$Li+K_2$ $\rightarrow$LiKK $\rightarrow$LiK+K	7.30 3.46	2.25 —	3.26 3.48	3.52 3.923
$Li+K_2$ $\rightarrow$KLiK $\rightarrow$KLi+K	9.73 —	4.68 —	3.45 —	3.45 —
$K+Na_2$ $\rightarrow$KNaNa $\rightarrow$KNa+Na	3.04 2.61	6.04 5.60	3.84 4.37	3.22 3.08
$K+Na_2$ $\rightarrow$NaKNa $\rightarrow$NaK+Na	0.88 —	3.87 —	3.70 —	3.70 —
$Na+K_2$ $\rightarrow$NaKK $\rightarrow$NaK+K	4.73 2.61	2.65 0.53	3.67 4.70	4.32 3.923
$Na+K_2$ $\rightarrow$KNaK $\rightarrow$KNa+K	5.95 —	3.87 —	3.64 —	3.64 —
$Rb+Na_2$ $\rightarrow$RbNaNa $\rightarrow$RbNa+Na	2.61 2.42	6.53 6.34	3.84 4.65	3.17 3.08
$Rb+Na_2$ $\rightarrow$NaRbNa $\rightarrow$NaRb+Na	— —	3.59 —	3.80 —	3.80 —
$Na+Rb_2$ $\rightarrow$NaRbRb $\rightarrow$NaRb+Rb	4.34 4.22	2.56 0.67	3.78 4.98	4.41 4.127
$Na+Rb_2$ $\rightarrow$RbNaRb $\rightarrow$RbNa+Rb	— —	3.61 —	3.83 —	3.83 —

a) $\mathit{\Delta}_r$ and $\mathit{\Delta}_p$ correspond to potential well depths with respect to reactants and products respectively. The upper and lower result in each row corresponds to linerar and isosceles triangular configurations respectively.

The ground (linear symmetric) state of alkali trimers can be further characterised by the force constants of its stretching and bending deformations. If R_{01} and R_{02}, and E_0 stand respectively for the internuclear distances and energy of the minimum energy intermediate state, then variation of energy around this state, to the lowest order is given by [34]

$$2(E-E_0) = A_{11}q_1^2 + A_{22}q_2^2 + A_{33}q_3^2, \tag{13}$$

where the terms q_i are defined as

$$q_1 = \frac{1}{2}[R_{ab}+R_{bc}-(R_{01}+R_{02})],$$

$$q_2 = \frac{1}{4}[(R_{01}+R_{02})^2-R_{bc}^2]^{1/2}, \tag{14}$$

and

$$q_3 = \frac{1}{2}(R_{ab}-R_{bc}),$$

q_1 describes a symmetrical stretching, q_2 a bending, and q_3 an asymmetric stretching motion. The coefficients

$$A_{ii} = \frac{\partial^2(E_0-E_i)}{\partial q_i^2} \tag{15}$$

are the corresponding force constants. As an illustration, we have calculated these force constants for the homonuclear trimers. These are given in Table 3.

TABLE 3. CALCULATED VALUES OF FORCE FOR THE GROUND STATE OF HOMONUCLEAR TRIMERS

Trimer	A_{11} (mdyn/Å) sym. stretching	$A_{22}\times 10$(mdyn/Å) asym. stretching	$A_{33}\times 10^3$(mdyn/Å) bending
Li_3	0.1293	0.3658	0.1264
Na_3	0.0857	0.2589	0.0406
K_3	0.0614	0.1415	0.0131
Rb_3	0.0486	0.1166	0.0119
Cs_3	0.0360	0.0995	0.0067

It can be seen from this table that the symmetric stretching force constants of the trimers are about half the magnitude of the force constants of the corresponding dimer. Again the asymmetric force constant which is important primarily in regard to "tunneling corrections" is almost one-fourth the magnitude of the symmetric force constant of an alkali trimer. Very low values of the bending force constant which determines the size of the (L, L_2) exchange cross-section near the threshold indicates that the rate of increase of potential energy as a complex is bent from the collinear conformation is very small.

Conclusion

For lack of experimental data on alkali trimers it is not possible to test the validity of the present calculation. However, because of the semi-empiricism of the method employed certain errors are likely to enter the calculations. The omission of three-centre integrals in London equation may be a possible source of error. Pedersen and Porter[35] have shown that the three-centre integrals in the calculation of H_3 complexes almost insignificantly contribute near the collinear saddle point. Similar trend may be expected to be followed also in the case of alkali complexes. Since in alkali atoms the np valence orbital is very close to the ns orbital we should have considered their effects in the calculations. However, the use of diatomic potential curves in the calculation of Coulomb and exchange integrals includes their effects to a certain extent. Whitehead and Grice considered the inclusion of overlap integral in their calculations of Q and J, and have shown that it increases the binding energy by about 2 kcal/mol. The inclusion of this integral effectively in the London equation seems not to be theoretically consistent. We have not, therefore, studied the same in the present calculations.

The most distinguishing feature of the present calculation is that only with the knowledge of three spectroscopic constants of a dimer one can now construct its potential energy surface with much less labour and computational expenses.

I am grateful to Professor H. N. Bose for his kind interests in the work.

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