

TABLE II. The static polarizability $\alpha(0)$ for alkali atoms.

Atom	$[2\alpha(0)]^{-1/2}$	Lowest core-excitation energy
Li	1.76	2.00
Na	0.72	1.15
K	0.30	0.71
Rb	0.21	0.59
Cs	0.17	0.50

our zero-order description of the transition, Eq. (6), is not a good approximation. The values of $[2\alpha(0)]^{-1/2}$ for alkali atoms⁵ are shown in Table II. Equation (16) would be satisfied for lower energies of transitions because $\alpha(\epsilon_{t_s}) > \alpha(0)$. The small-

est single-particle excitation energy of the core is also listed for each atom to show that excitations from the core are not important when the energy of transition satisfies Eq. (17).

It would be of great interest to know the variation of the correction $f^{(1)}$ with the energy of transition, for transitions from low-lying states, where penetration effects cannot be neglected. If the correction behaves as (16), even qualitatively, great caution is warranted in the calculation of photo-ionization cross sections.

ACKNOWLEDGMENTS

I wish to thank Professor S. F. Edwards and Dr. A. Herzenberg for their comments.

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PHYSICAL REVIEW

VOLUME 179, NUMBER 1

5 MARCH 1969

Bound States of Alkali and Noble-Gas Atoms*

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(Received 21 October 1968)

The numbers of bound states for mixtures of alkali and noble-gas atoms have been calculated for a 6-10 Lennard-Jones interatomic potential function. For this calculation, a simple analytic expression for the number of bound vibrational levels as a function of the angular-momentum quantum number has been obtained. Bound molecular states were found for all alkali-noble-gas atom pairs for which potential-function data are available. From these numbers of bound states, internal partition functions have been calculated and, finally, values obtained for the number densities of alkali-noble-gas molecules.

I. INTRODUCTION

In determining the properties of gas mixtures,

the degree of molecular association is of prime interest. We have considered here the interaction between an alkali and a noble-gas atom through a

Lennard-Jones type of potential. Thus they may bind together to form molecules: we use the term "molecule" to refer to a pair of atoms which possess at least one bound state within their interatomic potential well. We have calculated two properties of such molecules: (1) the number of vibrational and rotational bound states for each pair of atoms for which data are available for their Lennard-Jones potential, and (2) the statistical fraction of such molecules present in a gas of alkali and noble-gas atoms. We note that the calculation of these two quantities just takes 1 min by slide rule, and also emphasize that the method is applicable to any pair of atoms which interact by a Lennard-Jones potential.

The technique which we use to calculate the number of vibrational and rotational bound states is easily described in this introductory paragraph.¹ Let l denote the relative angular momentum of the alkali and noble-gas atoms. Then calculate the dimensionless constant

$$\eta_l = \frac{5}{8} \left[\left(\frac{1}{3}\beta \right)^{1/2} - 1 \right] - \frac{1}{4}l, \quad (1.1)$$

$$\text{where } \beta = \epsilon_0 \mu R_m^2 / \hbar^2. \quad (1.2)$$

The Lennard-Jones potential has maximum depth ϵ_0 at an interatomic separation of R_m , and μ is the molecular reduced mass. The number of bound vibrational states Ω_l with angular momentum l is obtained by rounding η_l off to the next-highest integer. For example, if $\eta_l = 1.4$, then $\Omega_l = 2$. If $\eta_l < 0$, then no bound states exist. This simple prescription is mathematically exact for a (6-10) Lennard-Jones potential. The justification for this simple procedure is given in Sec. II. There we discuss why the (6-10) potential is used rather than the (6-12) or some other popular form. In Sec. III we show that, for $l = 0$, the Morse potential predicts a number of bound states quite similar to (1.1) and (1.2).

For most conditions of experimental interest, it is also easy to calculate the fraction of bound molecules in a gas of alkali and noble-gas atoms. Most experiments are done at elevated temperatures, where kT is much greater than ϵ_0 . This means that all of the various bound states have an equal probability of being occupied. In this case, the internal partition function Q_{AN}^* for the molecule just equals the sum over all bound levels, i. e., it equals the number of bound levels

$$Q_{AN}^* = 2 \sum_{l=0}^{l_{\max}} (2l+1)\Omega_l.$$

The factor of 2 is spin degeneracy, $(2l+1)$ is orbital degeneracy, and Ω_l is the number of vibrational levels calculated above. The maximum value of angular momentum l_{\max} is the maximum value of l such that $\eta_l > 0$ in (1.1). The partition

function Q_{AN}^* is easy to evaluate, and one can thereby determine the fraction of molecules in a gaseous mixture. The details are presented in Sec. IV.

Details of bound states for alkali-noble-gas molecules are of particular interest in the study of satellite bands associated with atomic lines,² which result from close encounters between the alkali atoms (or other active species) and the noble-gas atoms (or other foreign species). One type of explanation for certain of these bands relies upon a molecular model, and therefore requires: (1) the existence of bound states, and (2) an estimate of the molecular concentration, which is based upon counting the number of these bound states. Other explanations of satellite bands which do not require bound states in their development are, of course, also possible. These have been quite successful in some cases, and it is not our intention to choose sides in these approaches. However, it is reasonable to assume that both these approaches have merit for the full explanation of satellite bands. It is therefore our intention to provide in this paper calculations of the number of bound states and the molecular composition for alkali-noble-gas systems for use in the development of molecular models. Some earlier calculations of these properties have appeared in the literature, but these have not resulted in simple relations of general use nor have they had the benefit of recent potential-function data.

II. THE NUMBER OF BOUND STATES

An alkali atom has an attractive interaction with a noble-gas atom. This is conventionally represented as a potential $V(R)$, where R is the separation of the two atomic centers. Molecular-beam scattering experiments have been successful in determining the magnitude of this potential for a wide variety of diatomic systems. The data are often presented in terms of a 6- n Lennard-Jones potential

$$V_n = \epsilon_0 \left(\frac{6}{n-6} Z^{-n} - \frac{n}{n-6} Z^{-6} \right), \quad Z = R/R_m, \quad (2.1)$$

where ϵ_0 is the maximum depth of the potential for angular-momentum quantum number $l = 0$, and R_m is the atom separation at this maximum depth. This potential has a long range R^{-6} attractive part plus a Z^{-n} ($n > 6$) repulsive core. Bernstein and Muckerman³ comment that the data are best fit by the choice $n = 8$ or $n = 12$.

Given this potential, the two atoms may be able to form a bound state with a number of vibrational and rotational levels. Here we wish to determine the number of these vibrational and rotational bound states.

We assume that the Born-Oppenheimer approxi-

mation is valid. Since the potential is spherically symmetric, we need to solve the radial part of Schrödinger's equation

$$\left[\frac{-\hbar^2}{2\mu R} \frac{\partial}{\partial Z} \left(\frac{1}{Z^2} \frac{\partial}{\partial Z} Z^2 \frac{\partial}{\partial Z} - \frac{l(l+1)}{Z^2} \right) + V_n(R) - E \right] \psi = 0, \quad (2.2)$$

where μ is the reduced mass. This equation cannot be solved for the potentials V_n of interest. Nevertheless, the number of bound states can still be determined accurately. For this we use the method of Schey and Schwartz.¹

These authors point out that the number of bound states can sometimes be determined even though one cannot solve the Hamiltonian of interest. Their method consists of solving the desired Hamiltonian for $E=0$. If this is possible, the number of bound states can be determined. This method provides neither the energies nor the wave functions of these bound states; it just provides information on the number of such bound states.

In order to see how the method works, let us rewrite our Hamiltonian in the form

$$[-(\hbar^2/2\mu)\nabla^2 + gV(R) - E]\psi = 0.$$

The dimensionless coefficient g indicates the strength of the potential. Assume that the potential $V(R)$ has attractive regions so that bound states can exist. Now consider the bound states which occur as g takes on different values. As shown in Fig. 1, there are no bound states for $g=0$. As the strength of the potential increases from zero, there is a value g_1 at which the first bound state appears for the potential. At $g=g_1$, the binding energy of this bound state E_1 is zero, and as g increases the state becomes more bound as E_1 increases in magnitude. Similarly, at a higher value of coupling strength g_2 the second bound state appears, and also increases in binding energy as the value of g is increased further. As the strength of the potential is increased further, additional bound states appear in succession.

Suppose that the actual potential we wished to solve has a strength g' . In the example shown in Fig. 1, there are five bound states at this value. This is also the number of $E=0$ bound states which exist for $g < g'$. Thus, if we are able to solve the Hamiltonian for $E=0$, we can thereby determine the number of bound states allowed for any value of coupling strength g .

This method does not work for Coulomb potentials of the type $-g/r$. This potential has an infinite number of bound states for an arbitrarily weak value of g . The method only is applicable if the potential has a finite number of bound states and works well for the Lennard-Jones potential of interest here.

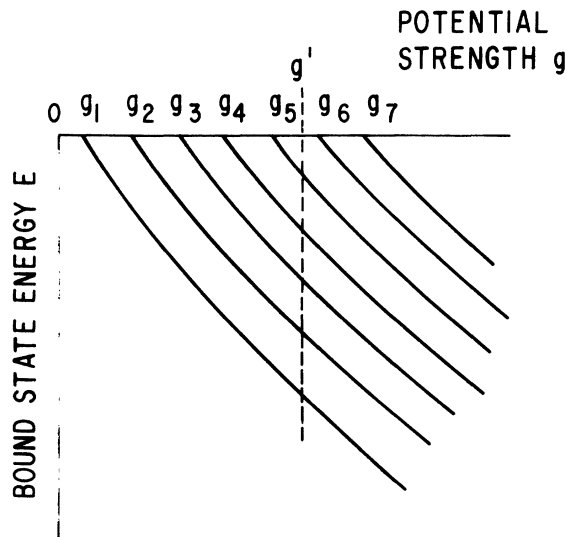


FIG. 1. A schematic representation of the change in the number and energy of bound states as the strength of the potential g is increased.

The Hamiltonian (2.2) can be solved for $E=0$ if we use a Lennard-Jones potential with $n=10$. Although this is neither the $n=8$ nor $n=12$ values which are of most interest, the case $n=10$ is certainly of the right magnitude to be of significance. The fact that only $n=10$ is solvable is a mathematical accident with no physical significance. An important feature of this technique is that it works for all values of angular momentum l .

We define a dimensionless parameter

$$\beta = \epsilon_0 \mu R^2 / \hbar^2,$$

and our Eq. (2.2) is, with $X=Z\psi$ and $E=0$

$$\left[\frac{\partial^2}{\partial Z^2} - \frac{l(l+1)}{Z^2} - \beta \left(\frac{3}{Z^{10}} - \frac{5}{Z^6} \right) \right] X = 0.$$

Set $y=Z^{-4}$, which transforms it into

$$\left(\frac{\partial^2}{\partial y^2} + \frac{5}{4y} \frac{\partial}{\partial y} - \frac{l(l+1)}{16y^2} - \frac{3}{16}\beta + \frac{5}{16}\frac{\beta}{y} \right) X(y) = 0.$$

This is a confluent hypergeometric equation with a solution⁴

$$X(y) = A e^{-ky} y^\lambda F\left(\frac{1+\lambda-\lambda'}{2} - \Delta; 1+\lambda-\lambda'; 2ky\right) + B e^{-ky} y^{\lambda'} F\left(\frac{1+\lambda'-\lambda}{2} - \Delta; 1+\lambda'-\lambda; 2ky\right)$$

where $\lambda = \frac{1}{4}l$, $\lambda' = -\frac{1}{4}(l+1)$,

$$\Delta = \frac{5}{8}(\beta/3)^{1/2}, \quad k = \frac{3}{4}(\beta/3)^{1/2}.$$

The condition that the wave function be well behaved at $R \rightarrow \infty$ ($Z \rightarrow \infty$, $y \rightarrow 0$) requires that $B=0$.

The confluent hypergeometric function is

$$F(a; b; Z) = 1 + \frac{aZ}{b} + \frac{a(a+1)}{b(b+1)} \frac{Z^2}{2!} + \frac{a(a+1)(a+2)}{b(b+1)(b+2)} \frac{Z^3}{3!} + \dots$$

If the series is allowed to continue to infinity, then F approaches the asymptotic value of $\Gamma(b)e^Z Z^{a-b}/\Gamma(a)$, or $\sim \exp(2ky)$ in our case. This causes the wave function to diverge as $R \rightarrow 0$ ($y \rightarrow \infty$). The divergence is avoided by causing the series to truncate at a finite number of terms. This is achieved by insisting that the parameter a be a negative integer or zero. For the present problem, this leads to the eigenvalue condition

$$-N = \frac{1}{2}(1 + \lambda - \lambda') - \Delta,$$

where N is a positive integer and where zero counts as an allowed integer. Rewriting this in our conventional notation,

$$N = \frac{5}{8}[(\beta/3)^{1/2} - 1] - \frac{1}{4}l.$$

According to the theory of Schey and Schwartz,¹ one gets an $E=0$ bound state whenever β and l are such that the right-hand side of this equation is an integer. For a given l value, the number Ω_l of bound vibrational states for a given value of β_0 equals the number of integers allowed for all values of $\beta \leq \beta_0$. This is just the value calculated on the right-hand side η_l after it is rounded off to the

next-highest integer. For example, if $\eta_l = 3.6$ there are four bound states corresponding to the integers 0, 1, 2, 3. Define

$$\eta_0 = \frac{5}{8}[(\beta/3)^{1/2} - 1]. \quad (2.3)$$

The number of bound states Ω_0 in an $l=0$ configuration is obtained by rounding off η_0 to the next-highest integer. Values of η_0 are presented in Table I for molecules of alkali-noble-gas systems. The first-two numbers in each set are R_m in Å and ϵ_0 in units of 10^{-14} erg. These values have been taken from Bernstein and Muckerman.³ Spaces left blank indicate that no experimental numbers are available for ϵ_0 and R_m . The third number is η_0 . Similarly, one can easily evaluate

$$\eta_l = \eta_0 - l/4, \quad (2.4)$$

which, when rounded off to the next-highest integer, gives the number Ω_l of bound states with angular momentum l . There are no bound states unless $\eta_l > 0$.

Values of Ω_l as a function of l for KAr molecules are presented in Fig. 2. The heavier molecules have more bound states because of their larger reduced masses μ and greater potential well depths ϵ_0 , the atom separation at the maximum well depth R_m remaining fairly constant.

III. COMPARISON WITH MORSE POTENTIAL

The Hamiltonian for the Morse potential can be solved exactly⁵ in the zero angular-momentum

TABLE I. Bound-state parameters for interactions between an alkali and a noble-gas atom. The two parameters R_m and ϵ_0 characterize the radius and depth of the Lennard-Jones potential. The quantity η_0 is defined in Eq. (2.3). By rounding η_0 off to the next-higher integer, one obtains the number of bound levels Ω_0 in the $l=0$ angular-momentum state.

	Ne	Ar	Kr	Xe	
Li	4.6	4.2	4.0	4.1	R_m (Å)
	0.19	0.92	1.5	2.4	ϵ_0 (10^{-14} erg)
	1.4	3.7	4.9	6.6	η_0
Na		4.1	5.0	4.9	
		1.0	1.4	2.1	
		6.3	10.5	13.3	
K	5.3	4.3	5.1	5.8	
	0.14	1.0	1.4	1.8	
	2.6	7.8	13.2	18.3	
Rb			4.4		
			1.6		
			15.3		
Cs		5.8	5.2	5.6	
		0.8	1.4	1.9	
		12.2	18.9	27.2	

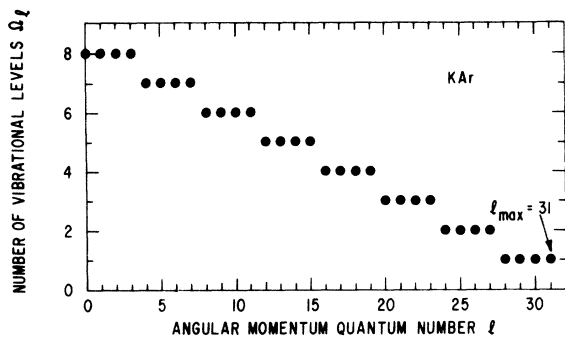


FIG. 2. The number of molecular levels Ω_l as a function of the angular-momentum quantum number l for KAr. Only levels up to the dissociation limit are counted.

state ($l=0$). Hence in this case one can also count the number of bound states. We have done this calculation in order to compare it with the results of the (6-10) potential. This comparison is only possible for the $l=0$ state, since the Morse potential is only solvable in this case. The great advantage of using the (6-10) potential is that one can count the number of bound states for all values of l .

The Morse potential can be written as

$$U(R) = A(e^{-2\alpha(R-R_0)} - e^{-\alpha(R-R_0)}).$$

In order that $U(R)$ have the same minimum energy ϵ_0 at the same radius R_m as our (6-10) potential, we require that $A = 4\epsilon$ and $\alpha = \ln 2 / (R_m - R_0)$. The potential $U(R)$ vanishes at $R = R_0$. For our comparison we have selected R_0 to be given by $Z_0 = R_0/R_m = (\frac{1}{2})^{1/6} = 0.866$. Figure 3 shows a comparison of this Morse potential with the (6-10) and (6-12) potentials. All three potentials are very similar.

Since the solutions to the Morse potential for $l=0$ are well known,⁵ we do not need to describe the derivation in detail. The bound states are at energies

$$E_n = -\epsilon \left[1 - \left(n + \frac{1}{2} \right) / (\gamma \sqrt{\beta}) \right]^2,$$

$$\gamma = (1 - Z_0) \sqrt{2} / \ln 2 = 0.273,$$

and where n can assume all integer values including zero such that the quantity in brackets is positive. The maximum value of n , found by setting the quantity in brackets equal to zero, is

$$n_{\max} = 0.273 \sqrt{\beta} - \frac{1}{2}, \quad (\text{Morse}).$$

The maximum value of n is n_{\max} rounded off to the next-lowest integer. Since $n=0$ is a bound state, the number of bound states is n_{\max} rounded off to the next-highest integer (as long as $n_{\max} > 0$). This should be compared with the results

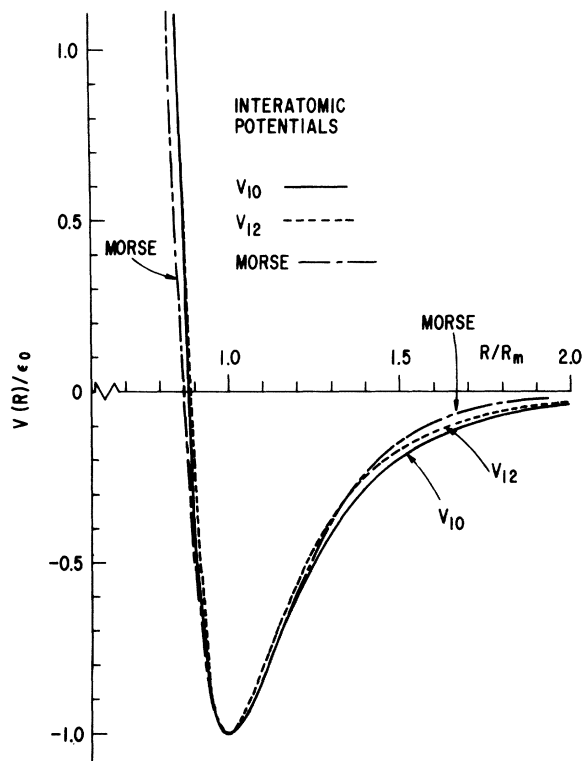


FIG. 3. Three interatomic potential functions. They are arranged to have the same maximum depth ϵ_0 occurring at the same radius R_m . The symbols V_{10} and V_{12} refer to the (6-10) and (6-12) Lennard Jones potential. The Morse potential is described in Sec. III.

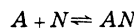
for the (6-10) potential in Eq. (2.3):

$$\eta_0 = 0.361 \sqrt{\beta} - \frac{5}{8}.$$

The two forms are remarkably similar: both have a square root of β dependence upon the basic parameters, and the numerical coefficients of 0.273 and 0.361 are similar. The Morse potential has fewer bound states, but this is reasonable since it falls off faster at large R (see Fig. 3). Thus we conclude that the Morse potential and (6-10) potential predict roughly equal numbers of bound states for $l=0$.

IV. THE NUMBER OF BOUND MOLECULES

Consider a gas mixture of two atomic species, A and N , where A is an alkali and N a noble gas. At a given temperature, we wish to determine the number of molecules AN which form according to the reaction



from the equilibrium constant. This equilibrium constant $K(T)$ may be evaluated through use of the numbers of bound states for the molecules which

were computed in the previous section. It is given by⁶

$$K(T) = n_{AN}/n_A n_N = (Q_{AN}/Q_A Q_N) e^{\epsilon_0/KT},$$

where n denotes the number of each species, Q the total partition function, and ϵ_0 the maximum well depth (i. e., dissociation energy for $l=0$). Here,

$$Q = \sum_j g_j e^{-E_j/kT}, \quad (4.1)$$

where the sum is to be evaluated over all energy levels j of statistical weight g_j and energy E_j . In turn, Q may be separated into translational and internal factors, Q' and Q^* , where

$$Q_A' = (2\pi m_A kT/h^2)^{3/2} V.$$

Thus

$$K(T) = \frac{n_{AN}}{n_A n_N} = \left(\frac{h^2}{2\pi\mu kT} \right)^{3/2} \frac{Q_{AN}^*}{Q_A^* Q_N^*} e^{\epsilon_0/kT} \quad (4.2a)$$

$$\approx \left(\frac{h^2}{2\pi\mu kT} \right)^{3/2} \frac{Q_{AN}^*}{Q_A^* Q_N^*}, \quad (4.2b)$$

where μ is the reduced mass of the AN molecule. In Eq. (4.2b), the exponential term has been omitted since it is close to unity for most conditions of experimental interest for the alkali-noble-gas systems. (Its neglect is consistent with the accuracy to be used in the calculation of the internal molecular partition function.) The maximum depth of the potential well ϵ_0 corresponds to about 100°K, whereas the optical experiments concerning these molecules are performed at temperatures greater than this by a factor of at least 4 (and, for the numerical calculations made later in this section, by a factor of 6.5).

The ground states of the alkali and noble-gas atoms are, respectively, 2S_g and 1S_g , which lead to the ground state $^2\Sigma^+$ for the AN molecule.⁷ For the atoms, $Q^* \approx g_0$, where the ground-state statistical weight g_0 is given by $(2J+1)$. Hence, $Q_A^* \approx 2$ and $Q_N^* \approx 1$.

For the calculation of Q_{AN}^* , we note that the exponential factors in Eq. (4.1) are close to unity because of the weak binding and, by their neglect, introduce the realistic approximation that all bound states have an equal probability of being occupied. In this approximation, Q_{AN}^* is just equal to the number of bound levels. In the previous sections, calculations were shown for the number of vibrational levels Ω_l corresponding to each allowed rotational angular-momentum quantum number l . The molecular internal partition function Q_{AN}^* is given by

$$Q_{AN}^* \approx \sum_l^{l_{\max}} (2J+1)\Omega_l,$$

where J is the total angular-momentum quantum number, including electron spin, and is a function of l (i. e., by summing over l , each algebraic value of J except J_{\max} is effectively counted twice in this case of a doublet, as will be seen below). For the molecular species in question, which correspond to Hund's case (b) for the coupling of angular momenta⁸ since there is no component of orbital angular momentum along the internuclear axis, we have $J = l + \frac{1}{2}$, $l - \frac{1}{2}$ (for $l \geq 1$). Thus

$$Q_{AN}^* \approx \sum_{l=0}^{l_{\max}} [2(l + \frac{1}{2}) + 1 + 2(l - \frac{1}{2}) + 1] \Omega_l$$

$$\approx 2 \sum_{l=0}^{l_{\max}} (2l+1)\Omega_l, \quad (4.3)$$

where Ω_l may be calculated from Eq. (2.4) and l_{\max} is determined by the condition that the minimum value of η_l is zero, which gives l_{\max} as the integer next lowest to $4\eta_0$. The summation in (4.3) may be evaluated by using the formulas given in the Appendix.

With the additional approximation for the usual experimental conditions that

$$p \approx n_N kT,$$

where p is the total system pressure, we finally obtain

$$\frac{n_{AN}}{n_A} \approx \frac{p}{kT} \left(\frac{h^2}{2\pi\mu kT} \right)^{3/2} \sum_{l=0}^{l_{\max}} (2l+1)\Omega_l. \quad (4.4)$$

The calculated values of the fraction of bound alkali atoms (n_{AN}/n_A) for the particular choice of $p = 1$ atm and $T = 374^\circ\text{C}$ are given in Table II along with the corresponding values of Q_{AN}^* computed from (4.3). For any alkali atom, this fraction increases greatly for interactions with the heavier noble gases. There is considerably less variation when one considers a single noble gas interacting with the various alkali atoms. The fraction of bound molecules scales linearly with pressure and to the $-(\frac{5}{2})$ power with temperature. These predictions could be checked experimentally.

V. DISCUSSION

The present calculation of the chemical equilibrium constant is considerably different from the usual one for molecules. In the usual case, the dominant temperature dependence is exponential. This is not the case here since the levels are so weakly bound. To a first approximation, all levels are equally occupied at the relevant experimental temperatures.

Another feature of the usual calculations is to

TABLE II. The quantity Q_{AN}^* is the number of different rotational and vibrational molecular bound levels. It is defined in Eq. (4.3). Also shown is the fraction of alkali atoms n_{AN}/n_A bound in molecules at $T=374^\circ\text{C}$ and a pressure of one atmosphere. It is assumed that the alkali atoms are dilute in the noble gas.

	Ne	Ar	Kr	Xe	
Li	0.0080	0.0808	0.176	0.405	Q_{AN}^* (units of 10^4)
	0.12	1.0	2.0	4.4	n_{AN}/n_A (units of 10^{-4})
Na		0.364	1.52	2.92	
		1.2	3.6	6.2	
K	0.0358	0.653	2.76	7.32	
	0.14	1.4	3.7	8.1	
Rb			4.36		
			2.9		
Cs		2.20	7.90	22.8	
		2.4	3.9	7.8	

separate the internal partition function into vibrational and rotational factors

$$Q_{\text{internal}}^* = Q_{\text{vib}}^* Q_{\text{rot}}^*$$

This cannot sensibly be accomplished in our case, since there is a strong interaction between the vibrational and rotational degrees of freedom. The weak binding accentuates the importance of the rotational potential-energy term, which significantly alters the potential shape as a function of the rotational quantum number l . Thus for different values of l , the vibrational levels are constructed from potential functions different enough to cause, for example, the characteristic average vibrational energy interval $[\epsilon_l/(\Omega_l - 1)] = hc\omega_l$ to vary strongly with l . (See Fig. 4.) Here, ω_l is the defined vibrational constant. For a harmonic oscillator, this parameter would be constant. The relatively modest number of allowed vibrational and rotational levels in this problem in any event do not permit the usual integral representations of the harmonic-oscillator vibrational partition function and rigid-rotor rotational partition function which result in simple analytic formulae.

One should be careful to distinguish between the real number of bound states and the effective number of bound states. We have just calculated the real number of bound levels, which are characterized by having an energy less than zero. However, let us consider the effective potential function

$$V_{\text{eff}} = V_n(Z) + (\hbar^2/2\mu R_m^2) l(l+1)/Z^2,$$

which we have schematically plotted in Fig. 5 for various values of l , where $Z = R/R_m$. For $E > 0$, there exist states where the two atoms are temporarily bound inside of the centrifugal barrier. Since the atoms can tunnel out of this barrier,

they are not true bound states but rather scattering resonances. But if they remain together for a sufficiently long time compared to collisional and radiative lifetimes, they can add significantly to the number of effective bound levels. Thus our calculated values of the fraction of alkali-noble-gas atom pairs bound as molecules represent lower limits.

One area of particular interest to which these calculations may be applied is the explanation of satellite bands,² which appear in the wings of

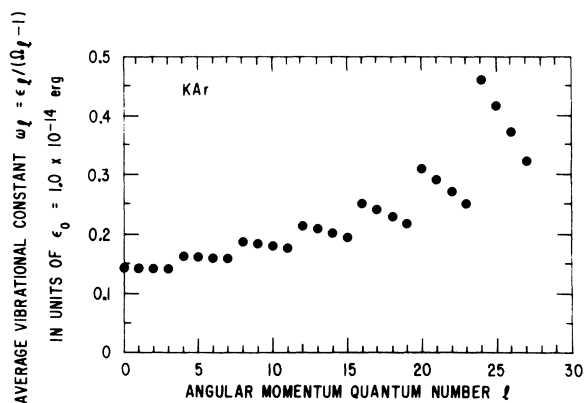


FIG. 4. Average vibrational constant (average spacing of vibrational levels) ω_l as a function of the angular-momentum quantum number l for KAr. Only levels up to the dissociation limit are considered. Here, ϵ_l is defined as the maximum depth of the effective potential. This estimate is intended only to illustrate roughly the variation of the vibrational constant with l . It is calculated according to the crude assumption that the vibrational levels are evenly spaced between the maximum well depth and the dissociation limit for each value of l . Since only one vibrational level exists for each value of l from 28 to 31 (l_{max}), the plot is terminated at $l = 27$.

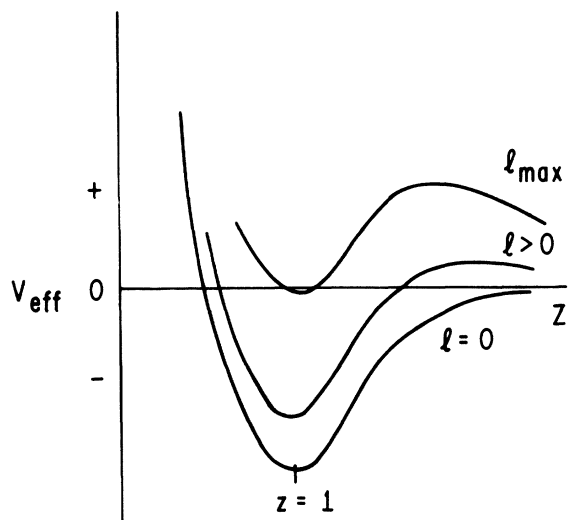


FIG. 5. A schematic diagram of the effective potential energy V_{eff} as a function of normalized interatomic distance Z , for various values of angular-momentum quantum number l .

atomic spectral lines due to perturbations caused by close encounters with foreign gases.

Explorations of satellite band formation have been made primarily in two fashions: (1) in terms of the shape of the potential function, without recourse to bound molecular states, and (2) in terms of molecular binding. Our work applies to the second of these approaches.

In pursuing the first approach, Jefimenko⁹ related alkali-noble-gas satellite bands to peculiarities in the potential curves; Kielkopf and Gwinn¹⁰ correlated red satellite band data for alkali-noble-gas atom pairs with a model based on a Lennard-Jones potential curve; and Farr and Hindmarsh¹¹ predicted red satellite bands for a radiating or absorbing atom perturbed by a foreign gas atom through use of the quasistatic theory of pressure broadening with a Lennard-Jones potential curve.¹²

Attempts to explain satellite bands in a molecular fashion, the second approach previously mentioned, have been considered by Klein and Margenau,¹³ who ascribed red satellite bands of alkali-noble-gas pairs to transitions from bound molecular levels¹⁴; Michels, de Kluiver, and ten Seldam,¹⁵ who found that violet satellite bands of mercury-noble-gas atom pairs could be explained on the basis of transitions from a bound molecular ground state; Herman and Herman,¹⁶ who ascribed various CsXe satellite bands to the molecular transitions $A^2\Sigma^+ - X^2\Sigma^+$ and $B^2\pi - X^2\Sigma^+$; and Takeo and Chen,¹⁷ on the other hand, who concluded that red satellite bands associated with Rb lines in the presence of Xe were not due to RbXe molecules in the electronic ground state.

In the course of their work, Klein and Margenau

estimated the fraction of alkali-noble-gas bound molecules through use of a statistical-mechanical argument with a Heller potential¹⁸ for which values of R_m were estimated. For an alkali-argon mixture at a density of 1 amagat (0°C and 1 atm), they found the fraction of molecular species to be 3.0×10^{-2} . Corrected to their conditions, our corresponding values range from 8.6×10^{-4} to 2.1×10^{-3} . If we consider that bound states for $V_{\text{eff}} \geq 0$ will increase our results by a factor of roughly 2, our values become 1.7×10^{-3} to 4.2×10^{-3} . Since these calculations were performed in a very different fashion and since considerably more accurate potential-function data are now available, the difference between these results is not surprising.

Michels *et al.* also performed a similar calculation for Hg noble-gas molecules. Their Eq. (3, 5'') is essentially the same as our Eq. (4.2a). Using a Heller potential and a numerical calculation of the energy levels of the HgAr molecule, they found the fraction of bound molecules $n_{\text{HgAr}} = 6.63 \times 10^{-3}$ at an argon density of 1 amagat. For rough comparative purposes, our value for CsAr (increased by a factor of 2 to account for the levels bound by the centrifugal barrier) is 4.2×10^{-3} , which is of the same magnitude. Michels *et al.* used approximately 3.3 Å for R_m and 4.8×10^{-14} ergs for ϵ_0 , yielding a value of $\beta = \epsilon_0 \mu R_m^2 / \hbar^2$ which is 2.1 times our value for CsAr. This indicates for purposes of comparison that our result for CsAr should be less than theirs for HgAr, as indeed it is, since the number of bound levels is proportional to $\beta^{1/2}$.

VI. CONCLUSION

A calculation of the number of bound states of alkali-noble-gas molecules is presented which results in a simple analytic expression dependent on the reduced mass, the depth of the potential well (taken to be a 6-10 Lennard-Jones potential), and the interatomic separation at the well maximum depth. All the alkali-noble-gas atom pairs for which potential-function data were available were found to have bound states, increasing (for angular orbital-momentum quantum number $l=0$) from 2 for LiNe to 28 for CsXe.

The fractions of bound molecules in alkali-noble-gas systems were also calculated at $T = 374^\circ\text{C}$ and $p = 1$ atm, resulting in values ranging from 10^{-5} for LiNe to 8×10^{-4} for CsXe, (omitting states effectively bound due to the centrifugal barrier).

Our estimates of the numbers of bound states of alkali-noble-gas molecules and the relative concentrations of these molecules do not prove the value of a specific approach to the solution of the general satellite band problem. However, the fact that molecular bound states exist for all the alkali-noble-gas pairs considered and that the

molecular concentrations may be easily estimated provides a firmer ground for those approaches based upon a molecular model. This work may be extended to other active atom-foreign-gas systems for the same purposes.

Note added in proof. F. Calogero and G. Cosenza [Nuovo Cimento, 45A, 866 (1966)] also discuss the number of bound states in Lennard-Jones potentials. Some of their results are similar to those in Sec. II.

APPENDIX: SUMMING THE NUMBER OF BOUND LEVELS

In Section IV we show that the internal partition function of the molecule can often be approximated by the expression

$$Q_{AN}^* = 2 \sum_{l=0}^{l_{\max}} (2l+1)\Omega_l .$$

Some simple analytical formulas for evaluating this summation are presented in this Appendix. Starting with the value for η_0 , which is some

number such as 3.14159..., we obtain Ω_0 by rounding up to 4. Four different formulas for evaluating Q_{AN}^* are required: one applies if the decimal part of η_0 is between 0.000... and 0.250..., the next between 0.250... and 0.500..., the third between 0.500... and 0.750..., and the fourth between 0.750... and 0.999... Let us express η_0 as $n.xxx\dots$, where n is the integer part and $xxx\dots$ is the decimal part. Then $\Omega_0 = n+1$. The four formulas are

$$n.000 < \eta_0 < n.250 \quad Q_{AN}^* = \frac{2}{3}\Omega_0(16\Omega_0^2 - 12\Omega_0 - 1), \quad (\text{A-1})$$

$$n.250 < \eta_0 < n.500 \quad Q_{AN}^* = \frac{8}{3}\Omega_0(4\Omega_0^2 - 1), \quad (\text{A-2})$$

$$n.500 < \eta_0 < n.750 \quad Q_{AN}^* = \frac{2}{3}\Omega_0(16\Omega_0^2 + 12\Omega_0 - 1), \quad (\text{A-3})$$

$$n.750 < \eta_0 < n.999 \quad Q_{AN}^* = \frac{16}{3}\Omega_0(\Omega_0 + 1)(2\Omega_0 + 1). \quad (\text{A-4})$$

Two examples: if $\eta_0 = 3.14159\dots$ then $\Omega_0 = 4$ and one uses (A-1); if $\eta_0 = 6.283\dots$ then $\Omega_0 = 7$ and one uses (A-2). These formulas are exact.

*Research supported by a National Science Foundation Grant 669GP7646.

†Alfred P. Sloan Research Fellow.

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