

Re, 73.4; F, 7.51. Found: Re, 74.2, 74.0; F, 7.61, 7.60; atomic ratio Re:F, 1.00.

**Boiling and Melting Points.**— $\text{ReO}_3\text{F}$ , sublimed a second time was refluxed in a glass tube, heated in a paraffin bath open to the atmosphere through a  $\text{Mg}(\text{ClO}_4)_2$  drying tube. It boiled at  $164^\circ$  at 760 mm. Slow decomposition occurred

during the measurement, as indicated by the formation of a dark residue.

The melting point determined in sealed capillary tubes was  $147^\circ$ .

PHILADELPHIA 40, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## The Possible Existence of a Reduced Potential Energy Function for Diatomic Molecules<sup>1</sup>

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A reduced potential energy is defined as  $V/D_e$  where  $V$  is the potential energy, taking the zero for infinite separation of the nuclei. A reduced internuclear distance is defined as  $(R - R_{ij})/(R_e - R_{ij})$  where  $R$  is the actual internuclear distance,  $R_e$  the equilibrium distance, and  $R_{ij}$  a constant for a given molecule formed from atoms  $i$  and  $j$ . It is shown that there exists an approximate universal relation, in the neighborhood of the minimum, between these variables for the ground states of a set of 23 diatomic molecules, chosen only for the accuracy of their experimental data.  $R_{ij}$  is interpreted as a measure of inner shell radii and is closely correlated with Badger's  $d_{ij}$ .

It is of interest to consider the possibility of a reduced potential energy function of diatomic molecules, *i.e.*, a relation between a "reduced" potential energy and a "reduced" internuclear distance, analogous to a reduced equation of state.

Let  $V$  be the potential energy of a diatomic molecule in the ground state or in any attractive excited state taking the zero of energy at infinite separation of the nuclei. Let  $R$  be the internuclear distance,  $R_e$  being the equilibrium value. At the potential energy minimum  $V = -D_e$  where  $D_e$  is the dissociation energy (including the half quantum of vibration). Now the simplest kind of reduced potential energy and distance would be defined as

$$V' = V/D_e \quad R' = R/R_e \quad (1)$$

in terms of which variables the P.E. minimum would be at  $V' = -1$  and  $R' = 1$  for every molecule. A reduced P.E. in this form  $V/D_e$  has been used by Puppi<sup>2a</sup> while Davies<sup>2b</sup> has used the reduced distance  $R/R_e$ . Puppi actually derived a reduced functional relation—his reduced distance variable being

$$y = \frac{R - R_e}{R_e \sqrt{D}}$$

This was obtained by assuming a Morse P.E. function and introducing an empirical relation equivalent to  $kR_e^2 = \text{a constant}$ , where  $k$  is the force constant. Puppi's reduced equation is not universal as  $kR_e^2$  remains constant only within small groups of molecules. Furthermore his variable  $y$  is complicated in that it mixes distance and energy.

The value of reduced variables as defined in (1) is shown in Figs. 1 and 2 where in Fig. 1,  $V$  is plotted *versus*  $R$  and in Fig. 2,  $V'$  *versus*  $R'$  for the ground states of  $\text{H}_2$  and  $\text{H}_2^+$ . Atomic units are used for Fig. 1. The variables of Fig. 2 are by definition dimensionless. The  $\text{H}_2$  curves are plotted according to the modified Morse function of Hulburt and Hirschfelder<sup>3</sup> while the  $\text{H}_2^+$  results are

the theoretical calculations of Burrau<sup>4</sup> and of Teller.<sup>5</sup>

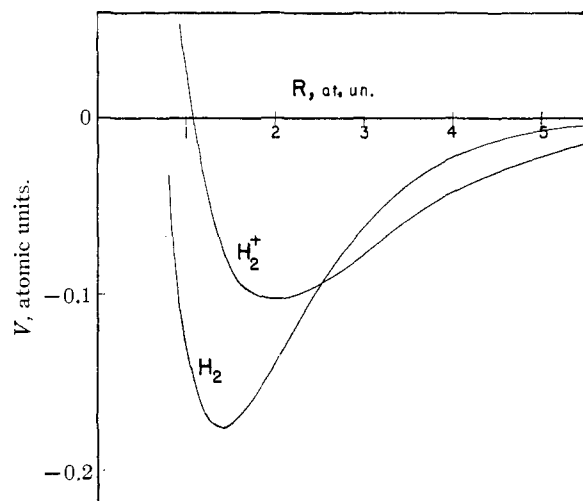


Fig. 1.—Potential energy curves for the ground states of  $\text{H}_2$  and  $\text{H}_2^+$ ; 1 atomic unit of energy = 27.2 e.v., 1 atomic unit of length = 0.529 Å.

**A More General Reduced Internuclear Distance.**—If P.E. functions for other than hydrogen molecules are plotted in Fig. 2 there is no general coincidence of curves. In particular, the curvature at the minimum, which is related to the force constant, may vary considerably from molecule to molecule. This is not surprising inasmuch as an inner shell repulsion for all atoms other than hydrogen should influence the internuclear distance at the minimum. To take this into account the definitions of equation 1 will be replaced by

$$V' = V/D_e \quad R' = (R - R_{ij})/(R_e - R_{ij}) \quad (2)$$

where  $R_{ij}$  is a constant for a given molecule and is a measure of inner shell radii of atoms  $i$  and  $j$ . Here, as before, the minimum is given by  $V' = -1$  and  $R' = 1$ .  $R'$  of (2) is identical with  $R'$  of (1) when  $R_{ij} = 0$  as it presumably is for  $\text{H}_2$  and  $\text{H}_2^+$ , there-

(1) A portion of this paper was presented at the Los Angeles Meeting of the American Chemical Society, March, 1953.

(2) (a) G. Puppi, *Nuovo Cimento*, **3**, 338 (1946); (b) M. Davies, *J. Chem. Phys.*, **17**, 374 (1949).

(3) H. M. Hulburt and J. O. Hirschfelder, *ibid.*, **9**, 61 (1941).

(4) O. Burrau, *Kgl. Danske Videnskab. Selskab.*, **7**, 1 (1927).

(5) E. Teller, *Z. Physik*, **61**, 458 (1930).

fore, Fig. 2 gives the functional relation for  $V'$  and  $R'$  of (2) as well as for (1).

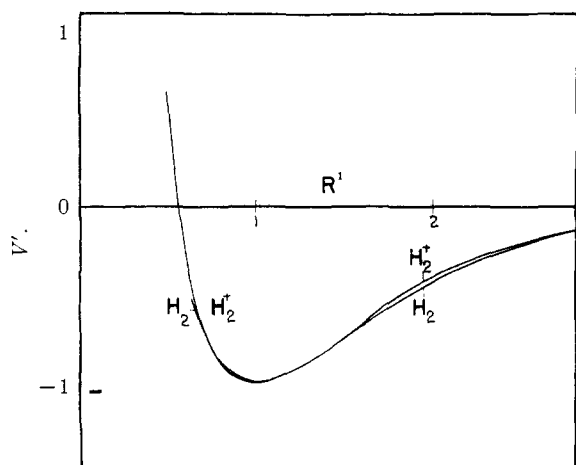


Fig. 2.—Reduced potential energy plot for ground states of  $H_2$  and  $H_2^+$ .

For other molecules than  $H_2$  and  $H_2^+$  the reduced P.E. curves cannot be plotted without knowing the  $R_{ij}$  values. It is apparent that an  $R_{ij}$  value could always be found which would make the curvature of the  $V'(R')$  curve at the minimum the same as for  $H_2$ . Instead of plotting such curves we shall assume that a universal function exists in the neighborhood of the minimum and derive from this a relation by which  $R_{ij}$  can be calculated from experimental results. If the so calculated  $R_{ij}$  values are in reasonable agreement with the idea of inner shell interaction this will constitute evidence in favor of the existence of a universal reduced P.E. function.

**Derived Relation Involving the Force Constant.**—Assume  $V'$  is a universal function of  $R'$  (of equation 2), independent of which molecule is being considered. At the minimum

$$\left(\frac{d^2 V'}{dR'^2}\right)_{R'=1} = K, \text{ a dimensionless constant}$$

Since the force constant for infinitesimal amplitude  $k_e = (d^2 V/dR^2)_{R=R_e}$ , it follows<sup>6</sup> that

$$k_e(R_e - R_{ij})^2/D_e = K \quad (3)$$

or that

$$R_{ij} = R_e - (KD_e/k_e)^{1/2} \quad (4)$$

To evaluate  $K$  let us first assume that for  $H_2$  and  $H_2^+$   $R_{ij} = 0$ . Then  $K$  may be calculated as  $k_e R_e^2/D_e$ . The result is  $K = 4.14$  for  $H_2$  and  $3.96$  for  $H_2^+$ , the similarity in values confirming the choice of  $R_{ij}$ . Now taking  $K = 4.00$  as a rounded average value,  $R_{ij}$  may be calculated for each molecule in any state. In Table I are given experimental data of  $k_e$ ,  $D_e$  and  $R_e$  for a number of molecules in their ground states and calculated values of  $R_{ij}$  from 4. The data are from Herzberg's tables<sup>7</sup> and include all molecules where values of all three experimental

(6) A referee of this paper has kindly called the authors' attention to the work of G. B. M. Sutherland, *J. Chem. Phys.*, **8**, 161 (1940), who has previously obtained a relation equivalent to (3). Although Sutherland assumed a special form of the potential energy function (double reciprocal type) his result may be considered as adding weight to the present more general argument.

(7) G. Herzberg, "Spectra of Diatomic Molecules," 2nd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1950.

quantities are considered to be accurately known. Inspection of the table shows that  $R_{ij}$  in general increases with periodic series classification as expected.

Also included in the table are values of Badger's  $d_{ij}$  for comparison.<sup>8</sup> Although his rule

$$k_e(R_e - d_{ij})^3 = \text{constant}$$

is purely empirical the similarity to our equation 3 leads one to expect a similarity in  $R_{ij}$  and  $d_{ij}$ . This similarity is demonstrated in Fig. 3 where it appears that to at least a crude approximation  $R_{ij}$  equals  $d_{ij}$ .

TABLE I

DIATOMIC MOLECULE DATA<sup>a</sup> AND CALCULATED RESULTS

Periodic series	Molecule	$k_e \times 10^{-5}$ , dynes/cm.	$D_e$ , e.v.	$R_e \times 10^3$ , cm.	$R_{ij} \times 10^3$ , cm.	$d_{ij} \times 10^3$ , cm.
0-0	$H_2^+$	1.575	2.788	1.06	-0.005	0.025
	$H_2$	5.73	4.745	0.7417	+0.02	
0-1	CH	4.45	3.65	1.1198	0.40	0.335
	OH	7.78	4.58	0.9706	0.35	
0-2	HCl	5.17	4.614	1.2746	0.52	0.585
	$HCl^+$	4.12	4.64	1.3153	0.47	
0-3	KH	0.562	1.92	2.244	0.77	0.650
	$ZnH$	1.511	0.949	1.5945	0.96	
	HBr	4.11	3.92	1.414	0.64	
0-4	CdH	1.205	0.765	1.762	1.13	...
	HI	3.139	3.198	1.604	0.80	
0-5	HgH	1.139	0.460	1.7404	1.23	...
1-1	$Li_2$	0.255	1.05	2.673	1.05	0.680
	$O_2$	11.77	5.178	1.2074	0.68	
	$O_2^+$	16.59	6.60	1.1227	0.62	
1-2	ClF	4.56	2.665	1.6281	1.02	0.94
2-2	$Na_2$	0.1717	0.74	3.079	1.42	1.25
	$P_2$	5.56	5.079	1.894	1.13	
	$Cl_2$	3.289	2.510	1.988	1.29	
3-3	$K_2$	0.0984	0.520	3.923	2.08	1.48
	$Br_2$	2.453	1.991	2.284	1.57	
2-4	ICl	2.381	2.176	2.321	1.56	1.48
4-4	$I_2$	1.723	1.555	2.667	1.91	1.76

<sup>a</sup> Data from G. Herzberg, ref. 7. To calculate  $R_{ij}$  from the data using equation 4  $D_e$  must first be converted into ergs per molecule by multiplying by  $1.602 \times 10^{-12}$ .

#### Additional Evidence from Anharmonicities.

The comparison of the previous section involves only the curvature of the minimum of the potential energy function. This is equivalent to a check up through the second degree term in a Taylor's series expansion of  $V$  as a function of  $R$  about the point  $R = R_e$  or of  $V'$  as a function of  $R'$  about the point  $R' = 1$ . A more complete test of the idea of a universal potential energy function is to test for constancy of the coefficients of higher powers such as  $L/6$  and  $M/24$  of the third and fourth degree terms of the latter expansion.

$$V' = -1 + \frac{1}{2}K(R' - 1)^2 + \frac{1}{6}L(R' - 1)^3 + \frac{1}{24}M(R' - 1)^4 + \dots \quad (5)$$

where

$$L = \left(\frac{d^3 V'}{dR'^3}\right)_{R'=1} \quad \text{and} \quad M = \left(\frac{d^4 V'}{dR'^4}\right)_{R'=1}$$

It is well known that the third derivative of a

(8) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

TABLE II  
DIATOMIC MOLECULE ANHARMONICITY DATA AND CALCULATED RESULTS<sup>a</sup>

Molecule	$\alpha_e, \text{cm.}^{-1}$	$\omega_e x_e, \text{cm.}^{-1}$	$-\left(\frac{d^3V}{dR^3}\right)_{R_e} \times 10^{-14}, \text{ergs cm.}^{-3}$	$\left(\frac{d^4V}{dR^4}\right)_{R_e} \times 10^{-23}, \text{ergs cm.}^{-4}$	$-L$	$M$	$R_{ij} \times 10^8 \text{ from } L, \text{cm.}$	$R_{ij} \times 10^8 \text{ from } M, \text{cm.}$	$(KM)^{1/2}/L$	$L^{1/3}/M$
H <sub>2</sub> <sup>+</sup>	1.4	62	0.712	0.2933	19.39	89.06	-0.005	-0.005	0.972	0.585
H <sub>2</sub>	2.993	117.995	3.70	2.34	18.76	86.82	+0.01	+0.01	.992	.575
CH	0.534	64.3	2.67	1.363	17.18	63.68	.38	.34	.928	.695
OH	.714	82.81	5.44	3.36	17.11	65.34	.33	.31	.944	.675
HCl	.3019	52.05	2.85	1.357	16.61	60.18	.49	.44	.931	.705
HCl <sup>+</sup>	.3183	53.5	2.30	1.092	18.92	76.77	.46	.43	.926	.657
KH	.0673	14.65	0.147	0.0253	15.49	39.74	.66	.43	.814	.972
ZnH	.2500	55.14	0.713	.1648	12.06	17.85	.85	.65	.702	1.550
HBr	.226	45.21	2.09	.884	15.71	51.92	.58	.52	.912	0.758
CdH	.218	46.3	0.566	.1778	11.82	23.68	1.02	.88	.819	1.140
HI	.183	39.73	1.558	.684	16.11	57.63	0.75	.70	.943	0.706
HgH	.312	83.01	0.656	.1790	11.63	16.21	1.14	.97	.689	1.627
Li <sub>2</sub>	.00704	2.592	0.0548	0.00854	13.96	35.46	0.87	.64	.853	0.948
O <sub>2</sub>	.01579	12.073	8.76	5.41	15.70	51.71	.64	.60	.912	.760
O <sub>2</sub> <sup>+</sup>	.01984	16.53	14.30	10.01	17.25	61.17	.60	.57	.904	.729
ClF	.00436	4.0 <sup>a</sup>	2.66	1.506	14.26	49.6	.96	.93	.987	.698
Na <sub>2</sub>	.00079	0.726	0.0314	0.00275	12.13	17.73	1.15	.60	.693	1.572
P <sub>2</sub>	.00142	2.804	2.652	.954	14.69	40.74	1.06	.96	.870	0.883
Cl <sub>2</sub>	.0017	4.0	1.838	.607	15.42	35.75	1.24	1.12	.773	1.073
K <sub>2</sub>	.000219	0.354	0.0156	.000887	11.61	12.17	1.76	.91	.599	2.165
Br <sub>2</sub>	.000275	1.07	1.058	.2533	12.45	21.68	1.46	1.26	.750	1.333
ICl	.000536	1.465	1.123	.421	14.38	41.44	1.48	1.40	.895	0.845
I <sub>2</sub>	.000117	0.6127	0.775	.2616	13.70	35.40	1.82	1.71	.868	0.927
Av.					15.06	43.48			0.855	0.982
% dev.					13.2	42.0			10.3	31.8

<sup>a</sup> Data for  $\alpha_e$  and  $\omega_e x_e$  from Herzberg, ref. 7.  $\omega_e x_e$  for ClF taken as 4.0 since value of 9.9 yields negative fourth derivative.

diatomic molecule potential energy function is related to the spectroscopic constant  $\alpha_e$  and the fourth derivative to both  $\alpha_e$  and to  $\omega_e x_e$  as follows.<sup>9</sup>

If  $V$  is expressed as the power series

$$V = -D_e + a_0 \xi^2 [1 + a_1 \xi + a_2 \xi^2 + \dots] \hbar c \quad (6)$$

with

$$\xi = \frac{R - R_e}{R_e}$$

then

$$a_1 = -1 - \alpha_e \omega_e / 6B_e^2 \quad (7)$$

and

$$a_2 = \frac{5}{4} a_1^2 - \frac{2}{3} \frac{\omega_e x_e}{B_e} \quad (8)$$

where  $\omega_e$  and  $B_e$  are the usual spectroscopic constants.<sup>6</sup> Also by differentiating (6)

$$\left(\frac{d^3V}{dR^3}\right)_{R=R_e} = \frac{3a_1}{R_e} \left(\frac{d^2V}{dR^2}\right)_{R=R_e} \quad (9)$$

$$\left(\frac{d^4V}{dR^4}\right)_{R=R_e} = \frac{12a_2}{R_e^2} \left(\frac{d^2V}{dR^2}\right)_{R=R_e} \quad (10)$$

and by comparing with (5) and (2)

$$L = \frac{(R_e - R_{ij})^3}{D_e} \left(\frac{d^3V}{dR^3}\right)_{R=R_e} \quad (11)$$

$$M = \frac{(R_e - R_{ij})^4}{D_e} \left(\frac{d^4V}{dR^4}\right)_{R=R_e} \quad (12)$$

Table II lists for the same molecules as in Table I experimental values of  $\alpha_e$  and  $\omega_e x_e$  and calculated results for  $L$  and  $M$  using the  $R_{ij}$  values of Table I. The mean deviation of  $L$  and  $M$  from their averages, 13.2 and 42.0%, respectively, agree with the

(9) See ref. 3 and also J. L. Dunham, *Phys. Rev.*, **41**, 721 (1932).

existence of an approximate universal relation. Although these deviations are too large to warrant quantitative predictions there is significance to this result as shown by the fact that the experimental quantities  $k$ ,  $D_e$ ,  $R_e$ ,  $\alpha_e$  and  $\omega_e x_e$  individually vary through anywhere from a fivefold range to a thousand-fold range as seen in Tables I and II.

Other columns of Table II show further tests of universality.  $R_{ij}$ 's may be calculated from equations 11 and 12 assuming constant values of  $L$  and  $M$ . As done in the calculation for Table I it is only natural to choose  $L$  and  $M$  such that  $R_{ij}$  for H<sub>2</sub> and H<sub>2</sub><sup>+</sup> are near zero.  $L$  is taken as -19.0 and  $M$  as 88.0 (both dimensionless). The resulting  $R_{ij}$  again follow more or less the periodic series classification. The  $R_{ij}$  from  $L$  indeed show a closer fit to the line of Fig. 3 than those plotted there.

Additional tests are obtained by calculating various combinations such as  $K^2/M$ ,  $K^{3/2}/L$ ,  $L^{1/3}/M$ , and  $(KM)^{1/2}/L$ . In all of these the  $R_e - R_{ij}$  cancels out so that no assumption has to be made concerning the  $R_{ij}$ . Also for the last quantity  $(KM)^{1/2}/L$  the  $D_e$  is cancelled so that the quantity depends only upon  $k$ ,  $\alpha_e$  and  $\omega_e x_e$ . It is seen from the table that  $(KM)^{1/2}/L$  has an average deviation of 10.3% and  $L^{1/3}/M$  of 31.8%.

### Discussion

It could hardly be expected that a universal reduced potential energy function would exist with any precision for all molecules and all states. There are too many known complexities such as differing natures of electronic spectroscopic states,

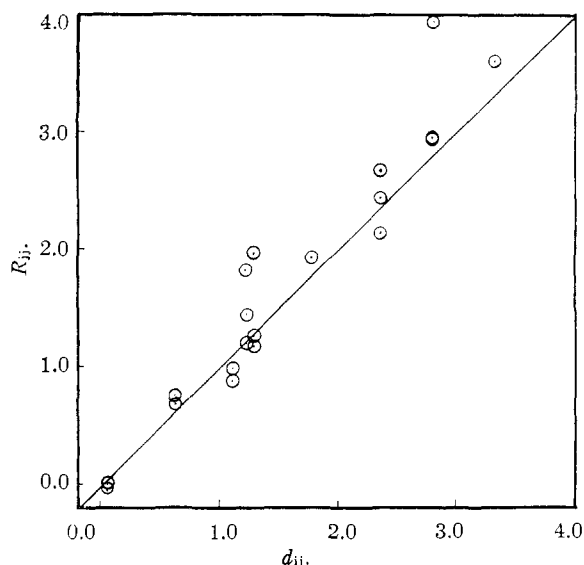


Fig. 3.—Plot of  $R_{ij}$  versus  $d_{ij}$ ; distance in atomic units, 1 atomic unit of length = 0.529 Å.

or especially the existence of ionic states where the potential energy at large distances would behave quite differently. Also perturbations between states may interfere. Nevertheless, it is evident that for a large group of states there is at least an approximate universal relation, at least in the neighborhood of the minimum.

It is at first disturbing that  $M$ , the fourth derivative in reduced variables, shows such a wide variation. However, it should be realized that this quantity is rather sensitive to the shape of the potential energy function and that the contribution of the corresponding fourth degree term in the expression for  $V'$  is relatively small. To show that  $M$  can vary considerably without greatly affecting the total potential energy there is plotted in Fig. 4  $V'$  versus  $R'$  as calculated from the fourth degree equation 5 using  $K = 4.0$  and  $L$  and  $M$  as listed in Table II. The curves include the case using average values shown as a full line together with the most extreme cases of Table II,  $H_2$  and  $K_2$ , shown as dashed lines. The close coincidence of the curves is a visual indication of just how good is the concept of a universal reduced potential energy function for the set of molecules considered here.

The treatment has been extended to some excited states with the same general results with

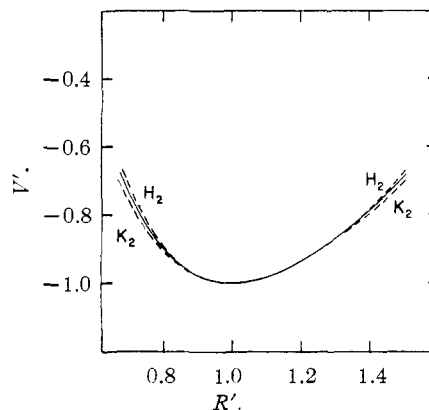


Fig. 4.—Plot of fourth degree reduced potential energy function: pull curve calculated with averaged constants; dashed curves for extreme cases of  $H_2$  and  $K_2$ .

certain striking exceptions. For example, calculation of  $K$  for the  $B$ ,  $C$  and  $E$  states of  $H_2$  assuming  $R_{ij} = 0$ , yields 1.59, 4.64 and 5.01, respectively. The  $B$  state value differs most strikingly from the previous value of 4.00. This perhaps is due to the fact that the  $B$  state is ionic.

It may be noticed that very few multibonded molecules are included in the list owing to uncertain  $D_e$  data. It is possible that the relations described in this paper might aid in choosing the appropriate value for a given molecule. Consider the cases of  $N_2$  and  $NO$ . For  $N_2$  the two values of  $D_e$  of 7.519 and 9.902 e.v. yield with equation 4  $R_{ij}$  values of 0.636 and 0.568 Å., respectively. For  $NO$  the  $D_e$  values of 5.41 and 6.61 e.v. yield  $R_{ij}$  values of 0.685 and 0.635 Å., respectively. In both cases the lower  $D_e$  value produces best agreement with the Badger  $d_{ij}$  value of 0.680 Å. However, this cannot be taken as strong evidence for the lower values of dissociation energies of these molecules as opposed to the currently favored higher values<sup>10</sup> inasmuch as other 1-1 series molecules in Table I show a wide variation of  $R_{ij}$  values.

**Acknowledgments.**—Thanks are due to R. L. Burwell, Jr., for suggestions and to Donald Cook for aid in calculation. This work was supported by a research grant from the National Science Foundation.

EVANSTON, ILLINOIS

(10) See review by G. Glockler in "Annual Review of Physical Chemistry," Vol. 3, Annual Reviews, Inc., Stanford, California, 1952, p. 158. Also M. H. J. Wijnen and H. A. Taylor, *J. Chem. Phys.*, **21**, 233 (1953).