INTERMOLECULAR POTENTIAL FUNCTIONS FOR NONPOLAR MOLECULES

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The potential energy curves appropriate for rare gas atoms have been analysed. Relative merits of these curves (in particular Morse hybrid potential functions) have been tested by calculating the values of the vibrational energy eigenvalue differences and comparing them with the experimental ones. Reliable estimates of the function parameters have been collected and compared with those obtained from molecular beam experiments.

Introduction

Knowledge of intermolecular forces is necessary for an understanding of many of the physical properties of rare gas systems. A number of recent studies, both theoretical and experimental, have contributed to this knowledge. The calculation of potential energy curves can in principle be accomplished by means of quantum mechanical calculations. However, computational difficulties prevent these curves from being calculated routinely for rare gas molecules. The short-range repulsive portion of these curves has been obtained from either Self-Consistent-Field or Thomas–Fermi–Dirac calculatios. In addition, the long-range attractive portion of these curves is known to have the form $-C_6r^{-6} - C_8r^{-8} - C_{10}r^{-10}$ [1]. In the last few years approximate theoretical calculations of the short-range repulsions [2–5] and accurate estimates for the C_6, C_8 and C_{10} coefficients for a variety of pairwise interactions of rare gas atoms have been reported [6–8]. Other advances have increased our knowledge of rare gas interactions. Potential energy curves have been obtained from *ab initio* calculations based on an electron gas model [9]. Also, *ab initio* potential curves for He_2 have been obtained [10–12]. The vacuum ultraviolet absorption spectra have been reported for a variety of rare gas systems [13, 38]. Molecular beam experiments have been carried out and the results have been analysed to obtain the potential energy curves of a number of combinations of rare gas atoms [34, 36, 37]. Other workers have produced semi-empirical potential functions by fitting a model potential form to experimental data.

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The primary difficulty with such semi-empirical schemes is in the choice of the potential function model.

In this paper we analyse the potential energy curves appropriate for the rare gas atoms. Relative merits of these curves have been tested by calculating the values of the vibrational energy eigenvalue differences and comparing them with the experimental values. Reliable estimates of the function parameters have been collected and compared with those obtained from molecular beam experiments.

Potential energy functions appropriate for rare gas atoms

The Lennard–Jones (12–6) potential has been widely used in the study of intermolecular forces [13–15]. This potential has the form:

$$U(r) = 4\varepsilon \left[\left(\frac{\delta}{r} \right)^{12} - \left(\frac{\delta}{r} \right)^{6} \right]. \tag{1}$$

Here ε and δ are parameters which represent an energy and a length which is characteristic of the system under consideration. This potential was widely used previously because of its simple analytic form, but has since been considered too inflexible to reproduce of dilute gas properties [17–21], therefore, some attempts to evaluate low density equilibrium and transport data have been directed towards finding more flexible functions [19]. Notable, among these are the Kihara potential [22]:

$$U(r) = 4\varepsilon \left[\left(\frac{\delta - 2a}{r - 2a} \right)^{12} - \left(\frac{\delta - 2a}{r - 2a} \right)^{6} \right] \quad r \geqq 2a \tag{2}$$

$$= \infty \qquad\qquad\qquad\qquad\qquad\qquad r \leqq 2a.$$

In Eq. 2 a third parameter "a" is added to represent the molecular core size, the Guggenheim–Mc Glasham potential [23], which introduces additional anharmonic terms in the neighbourhood of the potential minimum in order to explain solid properties, the formulation of BOYS and SHAVIT [24] which expands the potential in a complete set of Gaussian function, and the potential functions of DYMOND, RIGBY and SMITH [25] which represent the intermolecular energy by two-parameter in five terms, inverse power expression:

$$U(r) = \varepsilon \left[0.331 \left(\frac{r_m}{r} \right)^{28} - 1.2584 \left(\frac{r_m}{r} \right)^{24} + 2.07151 \left(\frac{r_m}{r} \right)^{18} - 1.74452 \left(\frac{r_m}{r} \right)^{8} - 0.39959 \left(\frac{r_m}{r} \right)^{6} \right] \tag{3}$$

where r_m is the intermolecular separation at the minimum energy $-\varepsilon$. The attractive term in r^{-24} has no theoretical basis but was found necessary to give a broad bowl to the potential function to fit experimental data. This potential gave a sound treatment of second virial coefficients and gave the correct lattice energies when used in conjunction with AXILROD's nonparwise corrections [26]. It also gave satisfactory agreement when applied to the calculation of third virial coefficients [25].

BUCKINGHAM [16,17] and BUCKINGHAM–CORNER [27] have proposed three parameter potential functions. These potentials are respectively given by:

$$U(r) = \varepsilon[\alpha/(\alpha-6)]\{(6/\alpha)\exp[\alpha(1-rr_m^{-1})] - r_m^6 r^{-6}\}, \tag{4}$$

$$U(r) = \varepsilon\left\{g_1(\alpha,\beta)\exp\left[\alpha\left(1-\frac{r}{r_m}\right)\right] - g_2(\alpha,\beta)\left(\frac{r_m}{r}\right)^6 \times \left[1+\beta\left(\frac{r_m}{r}\right)^2\right]\right\}, \quad r \geqq r_m. \tag{5}$$

$$U(r) = \varepsilon\left\{g_1(\alpha,\beta)\exp\alpha\left(1-\frac{r}{r_m}\right) - g_2(\alpha,\beta)\left(\frac{r_m}{r}\right)^6 \times \left[1+\beta\left(\frac{r_m}{r}\right)^2\right]\exp 4\left(1-\frac{r}{r_m}\right)^3\right\}.$$

$$r \leqq r_m.$$

$$g_1(\alpha,\beta) = (6+8\beta)/[\alpha(1+\beta)-(6+8\beta)],$$

$$g_2(\alpha,\beta) = \alpha/[\alpha(1+\beta)-(6+8\beta)],$$

where α is the parameter which is a measure of the steepness of the exponential repulsion. The parameters $\alpha, \beta, \varepsilon, r_m$ have been determined from the crystal data, second virial and the Joule–Thomson coefficient data. (The function of Eq. (4), in fact, is that portion of the modified Buckingham (exp–6) potential which is defined for $r \geqq r_{max}$. Here r_{max} is the position of the spurious maximum in the potential due to the unrealistic importance of the r^{-6} term for small r; r_{max} is the smallest root of $\exp[\alpha(1-r_m^{-1}r_{max})] = r_m r_{max}^{-1}$ [28]).

The success and failures of three-parameter potential functions are well known [29]. They have the advantage of their flexibility ·but two limitations, in particular, restrict their use for the prediction of data [30]. On the basis of the data available at this time one finds:

1. For any property, a set of parameters used to fit the data taken in a given temperature range cannot be relied upon to predict this property correctly in another temperature range.
2. A set of parameters used to fit one kind of property (*e.g.* viscosity) cannot be relied upon to predict correctly data for another property (*e.g.* second virial coefficient).

Furthermore parameters chosen with a model function do not always agree with values obtained from direct independent information such as the results of scattering experiments. Several authors have tried to remove the limitations of the three-parameters functions by proposing more elaborate potentials.

Successful examples are the semitheoratical Barker potential [31] and the *m*-6-8 potential based Barker one [30].

Barker function has the form:

$$U(r) = \varepsilon\left\{\exp[\alpha(1-r)]\sum_{i=0}^{3} A_i(r-1)^i - \sum_{l=0}^{2} C_{2l+6}/(\delta+r)^{2l+6}\right\}. \tag{6}$$

Here $r = R/R_m$, where R is the internuclear distance, R_m is the separation between atoms which corresponds to the minimum of the potential well, and ε is the value of the potential at its minimum. The C_6, C_8 and C_{10} coefficients are set equal to their calculated values. The remaining parameters are used to fit the function to

second virial coefficient data, molecular beam scattering measurements and low-pressure gas transport properties. The resulting potentials afford excellent agreement with a variety of experimental results other than those used in fixing their parameters. However, the method is limited by the large amount of experimental data which is needed.

Other semi-empirical schemes have been proposed by BERNSTEIN and MORSE [32], BRUCH and MC GEE [33] and KONOWALOW and ZAKHEIM [1]. These workers used a Morse function of the form:

$$U(r) = 4\varepsilon(y^2 - y),\tag{7}$$

$$y = \exp\left[c\left(1 - \frac{r}{\delta}\right)\right],$$

Here δ is the value of the separation of the nuclei such that $U(r) = 0$.

LEE [34] has proposed a hybrid potential function which he has fit to molecular beam scattering data. This potential is called the exponential-spline-Morse-spline-van der Waals (ESMSV) potential and has the following form:

$$f(x) = U(r)/\varepsilon, \quad x = r/r_m.$$

$$f(x) = A \exp\left[-\alpha(x-1)\right], \quad 0 \leq x \leq x_1.$$

$$f(x) = \exp\left(a_1 + (x-x_1)\{a_2 + (x-x_2)[a_3 + (x-x_1)a_4]\}\right),$$

exponential spline function, $x_1 \leq x \leq x_2$.

$$f(x) = b_1 + (x-x_3)\{b_2 + (x-x_4)[b_3 + (x-x_3)b_4]\},\tag{8}$$

spine function, $x_3 \leq x \leq x_4$.

$$f(x) = -C_6 r^{-6} - C_8 r^{-8} - C_{10} r^{-10}, \quad x_4 \leq x \leq \infty.$$

This potential gives good results for Ne_2 when compared with experimental data other than the solid state measurements from which its parameters were deduced [35]. For the heavier rare gas systems, instead of ESMSV potential, Morse-spline-van der Waals (MSV) potential [36, 38] was used. This potential has the form [36]:

$$f(x) = U(r)/\varepsilon,$$

$$f(x) = \exp\left[-2\beta(x-1)\right] - 2 \exp\left[-\beta(x-1)\right], \quad 0 \leq x \leq x_1.$$

$$f(x) = b_1 + (x-x_1)\{b_2 + (x-x_2)[b_3 + (x-x_1)b_4]\},\tag{9}$$

spline function, $x_1 \leq x \leq x_2$.

$$f(x) = -c_6 x^{-6} - c_8 x^{-8} - c_{10} x^{-10}, \quad x_2 \leq x \leq \infty,$$

where $c_i = C_i/\varepsilon r_m^i$.

Other workers have reported potential functions which are constructed from a Morse function, a long-range tail function, and an interpolating polynomial to join the two segments [5, 28]. KONOWALOW and ZAKHEIM [1] have reported Morse-6 hybrid potentials. Their potentials were constructed from three parts: 1) A short-range term of the form $U(r) = A \exp(-\lambda r)$, 2) a long-range dipole-dipole dis-

persion attraction $U(r) = -C_6 r^{-6}$, where the C_6 coefficients are obtained from highly accurate semiempirical estimates; 3) A Morse function of the form:

$$U(r) = \varepsilon \left\{ \exp\left[-2\frac{c}{\delta}(r - r_m) \right] - 2\exp\left[-\frac{c}{\delta}(r - r_m) \right] \right\}, \qquad (10)$$

which is used to connect the long and short-range segments.

Recently, KONOWALOW and co-workers described a modification of their procedure [41]. The term $-C_6 r^{-6}$ is replaced by $-C_6 r^{-6} - C_8 r^{-8} - C_{10} r^{-10}$, which is a more accurate representation of the long-range behaviour. The parameters A, λ, C_6, C_8 and C_{10} are available from theoretical calculations [3–8]. The other parameters: ε, c, δ or r_m, and q_0, where q_0 is the contact point between the Morse function and the long-range portion of the curve, are obtained by fitting second virial coefficient data.

Experimental second virial coefficient have traditionally been used in the study of intermolecular forces because of their ready availability and the ease at which they can be calculated for model potentials. The virial equation state for real gases is [14]:

$$pV_0 = RT(1 + B(T)/V_0 + C(T)/V_0^2 + \ldots),$$

where B and C are the second and third virial coefficients, respectively and V_0 is the molar volume. It is shown from statistical mechanics [14] that

$$B(T) = B_\Omega(T) + \frac{h^2}{m} B_1(T), \qquad (11)$$

where:

$$B_\Omega(T) = 2\pi N_A \int_0^\infty [1 - \exp(-U(r)/kT)] r^2 dr$$

and

$$B_1(T) = \frac{N_A}{24\pi k^3 T^3} \int_0^\infty \left(\frac{dU(r)}{dr} \right)^2 \exp(-U(r)/kT) r^2 dr$$

$B_\Omega(T)$ is the classical second virial coefficient and $B_1(T)$ is the first quantum correction to it. Here N_A is Avogadro number, k is Boltzman constant, h is Planck constant, m is the mass of the particle and $U(r)$ is some central field potential function. $U(r)$ is usually expressed in terms of a number of parameters.

In order to calculate the second virial coefficients at a given temperature T, the form of the potential must be specified. The potential under consideration has the form [41]:

$$U(r) = \varepsilon \left\{ \exp\left[-2\frac{c}{\delta}(r - r_m) \right] - 2\exp\left[-\frac{c}{\delta}(r - r_m) \right] \right\}, \quad 0 \leqq r \leqq q_0. \qquad (12)$$

$$U(r) = -C_6 r^{-6} - C_8 r^{-8} - C_{10} r^{-10}, \quad q_0 \leqq r \leqq \infty.$$

Another equivalent formula for the Morse potential is [1]:

$$U(r) = 4\varepsilon\left\{\exp\left[2c\left(1-\frac{r}{\delta}\right)\right] - \exp\left[c\left(1-\frac{r}{\delta}\right)\right]\right\}.$$

In order to determine the parameters $c, \delta, \varepsilon, C_6, C_8, C_{10}$ and q_0 KONOWALOW and co-workers applied the following procedure [41]: The C_6, C_8 and C_{10} coefficients set equal to their theoretical value. The repulsive portion of the Morse potential is set equal to the short-range repulsion [40] of the form: $A\exp(-\lambda r)$, where A and λ are obtained from quantum mechanical calculations.

$$A\exp(-\lambda r) = 4\varepsilon\exp\left[2c\left(1-\frac{r}{\delta}\right)\right].$$

Then

$$A = 4\varepsilon\exp(2c) \tag{13}$$

and

$$\lambda = 2c/\delta. \tag{14}$$

The parameter q_0 is found by finding the largest root of the equation:

$$-C_6 r^{-6} - C_8 r^{-8} - C_{10} r^{-10} - 4\varepsilon\left\{\exp\left[2c\left(1-\frac{r}{\delta}\right)\right] - \exp\left[c\left(1-\frac{r}{\delta}\right)\right]\right\} = 0.$$

The largest root is chosen because the long-range portion of the curve is valid only for large values of r. The parameter c is varied until the minimum of the difference between the sum of the squares of the calculated and experimental second virial coefficient is obtained. If c is obtained ε and δ can be calculated by means of Eqs. (13) and (14). The value of r_m is found by use of the relation:

$$r_m = (\delta/c)(c + \ln 2) \quad [42].$$

The parameters of the potential energy functions for nonpolar molecules were calculated without using the first quantum correction [41]. Here we include the estimates, where the first quantum correction was used in the calculation of the second virial coefficient also. From these potentials vibrational energy eigenvalue differences are calculated and are compared to experimental spectroscopic evidence [38, 39]. The function's parameters are compared to those obtained from various recent intramolecular potential calculations [1, 28, 30, 31, 41–58].

Empirical, semiempirical and theoretical parameters of the potential energy functions for nonpolar molecules

Reliable estimates of the parameters potential energy curves for nonpolar molecules are collected in Tables I–III.

Table I

Summary of parameters for the Lennard-Jones, Buckingham, Buckingham-Corner and Morse potential models for rare gas atoms*

Position	Potential function	System	Parameters				Method of calculation	Ref.
1.	Lennard-Jones (12-6) Eq. (1)		ε		r_m		Crystal data (CD)	[42]
		Ne-Ne	50.113		3.16			
		Ar-Ar	164.698		3.87			
		Kr-Kr	219.506		4.04			
		Xe-Xe	314.763		4.46			
2.	Buckingham (Exp-6) Eq. (4)		α	ε	r_m		CD, second virial coefficient (SVC) and viscosity coefficient	[27]
		Ne-Ne	14.5	52.460	3.147			
		Ar-Ar	14.0	170.082	3.866			
		Kr-Kr	12.3	218.539	4.056			
		Xe-Xe	13.0	319.181	4.450			
3.	Buckingham Corner (exp. 6-8) Eq. (5)		β	α	ε	r_m	CD and SVC	[17]
		Ne-Ne	0.2	13.9	51.218	3.87		
		Ar-Ar		13.6	170.082	3.16		
		Kr-Kr		11.7	219.230	4.08		
		Xe-Xe		12.8	324.703	4.45		
4.	Morse Eq. (7)		c	δ	r_m	ε	The combination of CD and SVC data	[42]
		Ne-Ne	5.1	2.775	3.152	60.729		
		Ar-Ar	5.0	3.386	3.855	199.902		
		Kr-Kr	4.5	3.510	4.038	252.224		
		Xe-Xe	4.9	3.872	4.420	379.234		

* ε in units of 10^{-23} J; δ and r_m in units of 10^{-10} m.

Discussion

Table III clearly shows the effect of adding higher-order terms in the long-range London dispersion potential. The effect of adding the C_8 and then the C_{10} term was to decrease the depth of the well as the additional terms were included. In addition the value of δ and r_m was increased by 0.0003–0.0004 nm with the addition of the C_8 term and by about 0.0001 nm with the addition of the C_{10} term to the $-C_6 r^{-6} - C_8 r^{-8}$ tail. The effect of adding the C_8 term to the $-C_6 r^{-6}$ tail is more pronounced than the addition of the C_{10} term to the tail which already includes the $-C_6 r^{-6} - C_8 r^{-8}$ term. Potentials which include the quantum corrections have smaller c values than those without this correction. The smaller c value implies that the well depth will be greater and that δ and r_m will be smaller for the potentials with the corrections. For example, in the case of Ar_2 the change in the well depth in the order of 1.38×10^{-23} J. (Values for the depth of the ground state potential well of Ar_2 and Kr_2 found from various intramolecular potential calculations [1, 28, 30, 31, 41–58] are summarized in Table IV.)

Table II
Summary of optimal parameters for the Morse-6 hybrid potential

System	No poten- tial	Parameters								Method of calculation	Ref.
		c	δ 10^{-10} m	r_m 10^{-10} m	ε 10^{-23} J	A 10^{-16} J	λ 10^{10} m^{-1}	C_6 10^{-26} J nm^6	q_0 10^{-10} m		
1	2	3	4	5	6	7	8	9	10		
Ne-Ne	1	6.0444	3.1993	3.5661	70.294	5.0011	3.7785	60.3012	6.0966	Parameters A, λ, C_6 from SCF calculations, other ones from second virial coefficient (SVC) data.	[1]
	2	6.0472	3.2007	3.5676	69.902	5.0011	3.7785	67.2884	5.9697		
	3	6.0276	3.1904	3.5572	72.696	5.0011	3.7785	0	5.9924		
	4	6.0014	2.7295	3.0447	67.714	4.4204	4.3974	60.3012	4.0945		
	5	6.0020	2.7298	3.0450	67.628	4.4204	4.3994	67.2884	3.8937		
	6	5.9433	2.7031	3.0183	76.059	4.4204	4.3974	0	4.0138		
	7	6.2574	2.6584	2.9529	73.256	7.9794	4.7075	60.3012	3.6621		
	8	6.2255	2.6449	2.9394	78.072	7.9794	4.7075	67.2884	3.4473		
	9	6.2048	2.6361	2.9306	81.380	7.9794	4.7075	0	3.5371		
	10	6.2015	2.6650	2.9629	72.012	6.9750	4.6541	60.3012	3.7066		
	11	6.1740	2.6532	2.9511	76.076	6.9750	4.6541	67.2884	3.4873		
	12	6.1468	2.6415	2.9393	80.339	6.9750	4.6541	0	3.5928		
	13	6.1696	2.6698	2.9696	71.285	6.5151	4.6218	60.3012	3.7383		
	14	6.1454	2.6593	2.9593	74.823	6.5151	4.6218	67.2884	3.5173		
	15	6.1137	2.6456	2.9456	79.727	6.5151	4.6218	0	3.6306		
Ar-Ar	1	5.8608	3.2323	3.6146	226.2981	11.1522	3.6264	622.1549	4.7456		
	2	5.8576	3.2305	3.6128	227.7476	11.1522	3.6264	663.3129	4.5866		
	3	5.8285	3.2145	3.5967	241.4150	11.1522	3.6264	0	4.6740		
	4	5.2046	3.3343	3.7783	196.1195	2.6013	3.1219	622.1549	5.8015		
	5	5.2077	3.3363	3.7803	194.9046	2.6013	3.1219	663.3129	5.6602		
	6	5.1742	3.3148	3.7589	208.3925	2.6013	3.1219	0	5.7336		
	7	5.8037	3.4179	3.8261	209.1656	9.1958	3.3961	622.1549	5.5912		
	8	5.8062	3.4194	3.8276	208.1302	9.1958	3.3961	663.3129	5.4733		
	9	5.7746	3.4008	3.8090	221.6871	9.1958	3.3961	0	5.5318		
	10	5.5020	3.4814	3.9200	195.7329	4.7064	3.1608	622.1549	6.1302		
	11	5.5945	3.4830	3.9216	194.7389	4.7064	3.1608	663.3129	6.0122		
	12	5.4765	3.4653	3.9039	205.9627	4.7064	3.1608	0	6.0634		
Kr-Kr	1	6.1843	3.4904	3.8816	325.9455	30.6722	3.5437	1225.1666	5.1371		
	2	6.1825	3.4894	3.8806	327.1051	30.6722	3.5437	1340.0260	4.9463		
	3	6.1588	3.4759	3.8672	343.0228	30.6722	3.5437	0	5.0056		
	4	5.1162	3.5906	4.0771	271.3865	3.0163	2.8497	1225.1666	6.5834		
	5	5.1195	3.5930	4.0795	269.5504	3.0163	2.8497	1340.0260	6.3880		
	6	5.0941	3.5751	4.0616	283.6181	3.0163	2.8497	0	6.4437		
Xe-Xe	1	6.2268	3.5434	3.9379	538.2725	55.1554	3.5140	2641.7656	4.7009		
	2	6.2071	3.5322	3.9267	559.9332	55.1554	3.5146	0	4.8711		

Table III

Summary of parameters for the Morse-6, -8, -10 hybrid potentials

System	No Pot.	c	δ 10^{-10} m	r_m 10^{-10} m	ε 10^{-23} J	A 10^{-16} J	λ 10^{10} m^{-1}	C_6 10^{-26} J nm^6	C_8 10^{-28} J nm^8	C_{10} 10^{-30} J nm^{10}	q_0 10^{-10} m	Method of calculation	Ref.
Ar-Ar	1	5.2075	3.3362	3.7802	194.9598	2.6012	3.1219	647.9983	3025.9683	0.0	5.5340	Parameters A, λ, C_6, C_8 C_{10}, from SCF calculations,* δ, c, r_m, ε, from SVC data without quantum corrections	[41]
	2	5.2087	3.3369	3.7810	194.5181	2.6012	3.1219	647.9983	3025.9683	18462.52	5.2436		
	3	5.8149	3.4245	3.8327	204.5408	9.1957	3.3961	647.9983	3025.9683	0.0	5.1819		
	4	5.8163	3.4253	3.8335	203.9610	9.1957	3.3961	647.9983	3025.9683	18462.52	5.0821		
	5	5.5065	3.4843	3.9229	193.9658	4.7064	3.1608	647.9983	3025.9683	0.0	5.8079		
	6	5.5071	3.4846	3.9232	193.7587	4.7064	3.1608	647.9983	3025.9683	18462.52	5.7574		
Kr-Kr	1	5.1159	3.5905	4.0769	271.4970	3.0163	2.8497	1273.0247	6630.8642	0.0	6.2277		
	2	5.1164	3.5908	4.0773	271.2347	3.0163	2.8497	1273.0247	6630.8642	46231.35	6.1694		
Ne-Ne	1'	5.9980	2.7280	3.0432	68.1724	4.3974	4.3974	62.6940	153.3085	0.0	3.5604		
	2'	5.9622	2.7117	3.0269	73.2335	4.3974	4.3974	62.6940	153.3085	523.8552			
	3'	6.1872	2.6286	2.9231	84.2930	7.9795	4.7075	62.6940	153.3085	0.0		SVC	
	4'	6.1914	2.6304	2.9249	83.5820	7.9795	4.7075	62.6940	153.3085	523.8552		with	
	5'	6.1296	2.6341	2.9319	83.1527	7.0147	4.6541	62.6940	153.3085	0.0		quantum	
	6'	6.1338	2.6359	2.9338	82.4514	7.0147	4.6541	62.6940	153.3085	523.8552		corrections	
	7'	6.0967	2.6338	2.9382	82.4720	6.5151	4.6218	62.6940	153.3085	0.0			
	8'	6.0967	2.6338	2.9382	82.4271	6.5151	4.6218	62.6940	153.3085	523.8552			
Ar-Ar	1'	5.2051	3.3346	3.7787	195.8986	2.6012	3.1219	647.9983	3025.9683	0.0	5.3619		
	2'	5.2062	3.3353	3.7794	195.4706	2.6012	3.1219	647.9983	3025.9683	18462.52	5.2536		
	3'	5.8120	3.4228	3.8310	205.7418	9.1957	3.3961	647.9983	3025.9683	0.0	5.1898		
	4'	5.8133	3.4236	3.8318	205.1758	9.1957	3.3961	647.9983	3025.9683	18462.52	5.0918		
	5'	5.5040	3.4827	3.9213	194.9322	4.7064	3.1608	647.0083	3025.9683	0.0	5.8133		
	6'	5.5046	3.4830	3.9216	194.7251	4,7064	3.1608	647.9983	3025.9683	18462.52	5.7633		
Kr-Kr	1'	5.1152	3.5900	4.0764	271.8697	3.0163	2.8497	1273.0247	6630.8642	0.0	6.2295		
	2'	5.1157	3.5903	4.0768	271.6212	3.0163	2.8497	1273.0247	6630.8642	46231.35	6.1714		

* The guide to the literature Ref. [1]

The effect of adding higher-order terms to the long-range portion of the potential on the vibrational energy levels of Ar_2 and Kr_2 we can see from Tables V–VI. These tables compare the vibrational spacings calculated from Morse hybrid potentials with experimental spectroscopic evidence [38, 39] and in the case of Kr_2 with the MSV scattering potential results [57]. Tables V–VI show that vibrational levels are predicted by all the present potentials which include a $C_8 r^{-8}$ term in the long range portion. The best results are obtained for the Morse hybrid 2′ (M-hybrid 2′) potential. Parameters of this potential are compared with experimental data in Table VII.

Table IV

Potential well depth ε [J] for Ar_2 and Kr_2

Ar_2			Kr_2		
Potential	$\varepsilon \cdot 10^{-21}$	Ref.	Potential	$\varepsilon \cdot 10^{-21}$	Ref.
Kihara	2.032	[43]	Kihara	2.959	[52]
Kihara	1.973	[44]	Kihara	2.977	[53]
Lennard—Jones(16-6)	2.056	[25]	Lennard—Jones (12-6)	2.366	[54]
Morse	1.831	[45]	Morse	2.527	[42]
exp-6	2.099	[43]	exp-6	2.959	[43]
Morse-6-hybrid	2.084	[1]	Morse-6-hybrid	2.700	[1]
M-6-8	2.112	[28]	M-6-8	2.715	[41]
M-6-8-10	1.955	[41]	M-6-8-10	2.712	[41]
Kingston	2.022	[46]	Dymond-Adler	2.716	[53]
Munn—Smith	2.112	[47, 48]	Rigid—Morse—		
Barker—Pompe	2.039	[31]	Mie—van der Waals	2.561	[56]
Dymond—Alder	1.908	[50]	Barker—Bobetic	2.725	[49]
Barker—Bobetic	1.936	[49]	MSV	2.746	[57]
Barker—Fisher	1.962	[51]	Gordon—Kim	2.485	[58]
Watts					
MSV	1.993	[36]			

Table V

Comparison of the experimental data for the vibrational spacings for the ground electronic state of Ar_2 with calculated from Morse hybrid potentials

v''	$G\left(v'+\frac{1}{2}\right)$ [cm^{-1}]						
	Experiment	1′	2′	3′	4′	5′	6′
0	25.4	24.364	24.338	27.162	27.124	24.607	24.594
1	20.2	20.246	20.224	22.570	22.539	20.447	20.437
2	15.5	16.111	16.094	17.961	17.936	16.272	16.263
3	10.3	11.676	11.664	13.017	12.999	11.792	11.787
4	7.99	6.946	6.939	7.744	7.733	7.015	7.012
5		3.697	3.693	4.121	4.115	3.733	3.731
6		1.465	1.464	1.633	1.631	1.480	1.479

Table VI

Comparison of the experimental data for the vibrational spacings for the ground electronic state of Kr_2 with calculated from Morse hybrid potentials and MSV scattering potentials.

v''	$G\left(v''+\frac{1}{2}\right)$ [cm^{-1}]				
	Experiment	1′	2′	MSV[a]	MSV[b]
0	21.56	20.995	21.015	21.17	21.39
1	19.09	19.237	19.229	19.15	19.26
2	16.76	17.479	16.237	16.86	16.81
3	14.76	15.719	14.602	14.65	14.74
4	12.23	13.961	12.969	12.69	13.10
5	10.49	12.201	11.334	10.80	11.07
6	8.92	10.437	9.700	8.96	9.00
7	6.92	8.662	8.050	7.12	7.11
8	5.54	6.671	6.200	5.38	5.42
9	4.09	4.412	4.10	4.01	3.94
10	2.87	2.982	2.77	2.83	2.69
11	1.86	1.819	1.69	1.80	1.68
12	1.07	0.968	0.90	1.00	0.90

[a] $r_m = 0.411$ [nm]
[b] $r_m = 0.403$ [nm] Ref. [38]

Table VII

Experimental results for Ar_2 and Kr_2

Substance	Potential	Parameters			Ref.
		$\varepsilon \cdot 10^{-21}$ J	r_m nm	δ nm	
Ar_2	Barker—Fisher—Watts	1.962	0.37612	0.33605	[51]
	MSV-II	1.993	0.3715	0.3330	[36]
	MSV-III	1.942	0.376	0.3354	[36]
	M-hybrid 2′	1.954	0.37794	0.3353	
Kr_2	Barker—Bobetic	2.725	0.40152	0.35944	[49]
	MSV	2.746	0.411		[57]
	M-hybrid 2′	2.716	0.40768	0.35903	

The comparison of the Morse hybrid potentials with experimental data and potentials obtained by other workers reveals that the method of calculation of the parameters of the Morse hybrid potential function is adequate for the heavier rare gas systems. For this reason Morse hybrid potentials appear to warrant further application in the description of van der Waals molecules. As a successful example we refer to the KONOWALOW–MUHLHAUSEN paper [59].

Acknowledgement

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ФУНКЦИИ МЕЖМОЛЕКУЛЯРНОЙ ПОТЕНЦИАЛЬНОЙ ЭНЕРГИИ ДЛЯ НЕПОЛЯРНЫХ МОЛЕКУЛ

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В данной работе обсуждается проблема кривых потенциальной энергии применимых для неполярных молекул. Правильность этих функций (прежде всего Морзе-гидридных кривых) доказывается сравнением вычисленных расстояний между осцилляционными уровнями с экспериментальными значениями. Результаты полученные для параметров межмолекулярных функций применимых для неполярных молекул собранье вместе с экспериментальными данными.