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A COMPARATIVE STUDY OF INTERMOLECULAR POTENTIAL ENERGY FUNCTIONS PROPOSED FOR THE RARE GAS DIMERS

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The vibration-rotation energy level spacings of homo- and heteronuclear rare gas dimers are calculated for some more common analytical intermolecular potential energy functions in a unified way by employing the discrete variable representation (DVR) method.

K e y w o r d s: rare gas dimers, DVR method, vibration-rotation energy levels.

INTRODUCTION

The dispersion interaction is the only contributor to intermolecular attractions in all spherically symmetric neutral species [1], such as rare gas dimers X···Y, where X, Y = He, Ne, Ar, Kr, Xe, Rn. The extremely shallow well (with a depth much smaller than the thermal energies at room temperature) in the potential curve $V(R)$ (where R is the intermolecular distance) at a relatively large intermolecular separation produced by the dipersion attractions is deep enough to allow the existence of dimers at low temperatures. Since the dispersion attraction increases as the atomic size increases, the well becomes deeper as the dimer size increases.

The detailed quantum mechanical calculations show that the dispersion interactions between two non-overlapping species vary as R^{-2n}, where $n = 3, 4, 5, \ldots$ corresponds to induced dipole-induced dipole, induced dipole-induced quadrupole, induced quadrupole-induced quadrupole, …, interactions respectively [2]. An accurate *ab initio* calculation of the dispersion interaction is rather complicated in such large basis sets and also high-level electron correlation treatments are required to reproduce the experimental data.

Suppose that the entire potential energy between two rare gas atoms is approximated as

$$V(R) \cong V_{\text{rep}}(R) - \sum_{n=3} C_{2n} R^{-2n}, \tag{1}$$

where C_6, C_8, C_{10}, … are the dispersion coefficients and $V_{\text{rep}}(R)$ is the repulsive contribution to the potential that in the simplest form can be represented by a Born-Mayer repulsive potential: $A\exp(-bR)$, in which A and b are the Born-Mayer parameters. However, the attractive part of this potential has an improper behavior in that it goes to $-\infty$ as $R \rightarrow 0$. This is due to the asymptotic nature of the dispersion expansion, which is only valid for the distances where charge distributions do not overlap, and thus lack of a term that accounts for the overlapping region. Furthermore, the entire potential shows an unphysical maximum at short internuclear distances. To eliminate these unrealistic behaviors we may either define a piecewise function by restricting the range of validity of the potential or introduce a damping function in the attractive part of the potential.

In the following we shall briefly describe some more common potential functions devised, by taking equation (1) as the starting point, for the inert gas dimers from experimental data or theoretical calculations.

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i. (Hartree-Fock-dispersion) HFD-B potential function [3—5]

$$V(R) = A\exp(-\alpha R + \beta R^2) - F(R)\sum_{n=3}^{5} C_{2n}R^{-2n} \tag{2a}$$

with a piecewise damping function of the type first used in the Buckingham-Corner potential [1]

$$F(R) = \exp[-(DR^{-1}-1)^2] \tag{2b}$$

for $R < D$ and $F(R) = 1$ for $R \geq D$ (where D is the damping parameter), has been parameterized for Ar$_2$, Kr$_2$, and Xe$_2$ dimers [6]. The parameters were determined by fitting $V(R)$ to the most accurate *ab initio* data points at the CCSD(T) level of theory using aug-cc-pV6Z basis set+(3s3p2d2f1g) bond functions + core correction for Ar$_2$, and ECP+aug-cc-pVQZ basis set+(3s3p2d2f1g) bond functions for Kr$_2$ and Xe$_2$. Also, the parameterization of HFD and HFD-B potentials has been carried out for the dimers HeKr, ArKr [4]; HeXe, HeAr [7]; and NeKr, NeXe [8].

ii. Murrell *et al*. potential function [9]

$$V(R) = A(1 + a_1R + a_2R^2 + a_3R^3)\exp(-a_4R) - f(R)\sum_{n=3}^{5} C_{2n}R^{-2n} \tag{3a}$$

with

$$f(R) = \tanh(R - R_e / 2), \tag{3b}$$

where the repulsive part is an extended Rydberg (ER) type potential, has been proposed for the ground state of 39 van der Waals dimers, including all homo- and heteronuclear inert gas dimers of He, Ne, Ar, Kr, and Xe, and for a few excited states. Using the available dispersion constants C_{2n}, the parameters of the ER repulsive potential were adjusted by a least squares fitting to the data points (in a given range) obtained from the best literature potentials. The function $f(R)$ for $R > R_e/2$, where R_e is the equilibrium internuclear distance, acts as a damping function and for $R > R_e/2$ contributes to the repulsive part of the potential. All constants in the potential given in this equation have been tabulated for all 39 dimers.

iii. Tang-Toennies(TT) potential function [10]

$$V(R) = A\exp(-bR) - \sum_{n=3}^{5} f_{2n}(bR)C_{2n}R^{-2n} \tag{4a}$$

with the damping function

$$f_{2n}(bR) = 1 - \exp(-bR)\sum_{j=0}^{2n} \frac{(bR)^j}{j!} \tag{4b}$$

has been parameterized for all the possible 21 homo-and heteronuclear rare gas dimers [11]. Using the available dispersion coefficients C_{2n} and the available (or estimated from the combining rules) well parameters, R_e and the depth, the Born-Mayer repulsive parameters A and b were determined by a fitting procedure. The dispersion constants as well as the well parameters for the heteronuclear Rn dimers were estimated from the combining rules. For Rn$_2$ the C_6 and C_8 were available and C_{10} was estimated from the empirical relation $C_{10} = 1.21C_8^2 / C_6$. The whole set of parameters have been tabulated for all 21 dimers.

iv. Eggenberger *et al.* potential function [12]

$$V(R) = A\exp(-bR) + aR^{-12} - \sum_{n=3}^{5} C_{2n}R^{-2n}, \tag{5}$$

where the repulsive part is the sum of Born—Mayer and the Lennard—Jones repulsive potentials, has been parameterized for the Ne—Ne interaction. All parameters were obtained by fitting $V(R)$ to the data points obtained from the MP4 [12], MP4 (SDTQ) [13] calculations, as well as to the experimentally determined values [14].

v. Korona *et al*. potential function [15]

$$V(R) = A\exp(-\alpha R + \beta R^2) - \sum_{n=3}^{8} f_{2n}(bR)C_{2n}R^{-2n}, \tag{6}$$

where $f_{2n}(bR)$ is the TT damping function, has been parameterized for all homo- and heteronuclear dimers of He, Ne, Ar, and Kr [16, 17]. For the most suitable set of dispersion constants, in which the higher constants C_{12}, C_{14}, and C_{16} were found from extrapolation formulas, the parameters α, β, A, b were determined by fitting the $V(R)$ to the most accurate *ab initio* calculated points at the CCDS (T) level of theory using the (aug-cc-pV5Z) basis set supplemented with a set of $(3s3p2d2f1g)$ bond functions, and counterpoise corrections. Another parameterization has been performed for heteronuclear dimers HeNe, HeAr, and NeAr using *ab initio* results at the CCSD (T) level of theory with aug-cc-pV6Z basis set+$(3s3p2d1f1g)$ bond functions [18].

The goal of this paper is to compare the spectroscopic data predictions of the various potential functions in equations (2)—(6) by performing a unified calculation of the vibration-rotation energy levels of homo- and heteronuclear rare gas dimers for each potential. To that end, the energy levels are found by diagonalizing the matrix of the Hamiltonian operator for the nuclear motion in the ground electronic state (X $^1\sum_g^+$ or X $^1\sum^+$) of a dimer

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + V(R) + \frac{\hbar^2 J(J+1)}{2\mu R^2} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + U(R) \tag{7}$$

in the so-called discrete variable representation (DVR) basis [19—23]. Here μ is the reduced mass and J is the rotational quantum number (ignoring the nuclear spin angular momentum if it is present). The DVR methodology for one-dimensional problems is described in the following section, and the results and discussion are presented further on.

DVR METHODOLOGY

Let $\hat{H} = \hat{T}(x) + U(x)$ be the Hamiltonian operator for a one-dimensional system (where x stands for a Cartesian or generalized coordinate) whose corresponding Schrödinger equation cannot be solved analytically.

A computationally efficient method to obtain good estimates for the eigenvalues (and the eigenvectors) of $\hat{H}$ is the diagonalization of the Hamiltonian matrix in so-called DVR basis functions. A DVR basis set is constructed from a set of the orthonormal basis functions $\{\varphi_0(x), \varphi_1(x), …, \varphi_{N-1}(x)\}$ as follows. Suppose there is a Gaussian quadrature with points $\{x_1, x_2, …, x_N\}$ and weights $\{w_1, w_2, …, w_N\}$ such that the orthonormality relations of the basis functions on the interval $[a, b]$ are given exactly

$$\delta_{kl} = \int_a^b \varphi_k^*(x)\varphi_l(x)dx = \sum_{\alpha=1}^N w_\alpha \varphi_k^*(x_\alpha)\varphi_l(x_\alpha) = (SS^\dagger)_{kl}, \tag{8}$$

where the $N \times N$ unitary matrix S is defined by $S_{k\alpha} = w_\alpha^{1/2}\varphi_k^*(x_\alpha)$. The unitarity of S implies that the quadrature points $\{x_1, x_2, …, x_N\}$ and weights $\{w_1, w_2, …, w_N\}$ have to fulfill the following relation:

$$\sum_{k=0}^{N-1}\varphi_k^*(x_\alpha)\varphi_k(x_\beta) = w_\alpha^{-1}\delta_{\alpha\beta}, \tag{9}$$

Furthermore, the orthonormal functions defined by

$$\Phi_\alpha(x) = \sum_{k=0}^{N-1} S_{k\alpha}\varphi_k(x) = w_\alpha^{1/2}\sum_{k=0}^{N-1}\varphi_k^*(x_\alpha)\varphi_k(x). \tag{10}$$

also called the Lagrange functions [23], form a DVR basis satisfying $\Phi_\alpha(x_\beta) = \delta_{\alpha\beta}/w_\alpha^{1/2}$, α = 1, 2, …, N.

Now suppose that the basis functions $\varphi_k(x)$ can be defined as $\varphi_k(x) = \sqrt{w(x)}P_k(x)$, where $\{P_k(x)\}$, $k = 0, 1, …, N-1$ is a set of orthonormal polynomials (such as Hermite, Laguerre, Legendre, etc.) on the interval $[a, b]$ with respect to a weight function $w(x)$. These functions satisfy the Christoffel-Darboux indentity [24]

$$\sum_{k=0}^{N-1}\varphi_k(x)\varphi_k(y) = \frac{k_{N-1}}{k_N}\frac{\varphi_N(x)\varphi_{N-1}(y) - \varphi_{N-1}(x)\varphi_N(y)}{x-y}, \tag{11a}$$

where k_n is the coefficient of x^n in $P_n(x)$. In the limit $y \to x$, this identity becomes

$$\sum_{k=0}^{N-1} \varphi_k(x)\varphi_k(x) = \frac{k_{N-1}}{k_N}[\varphi'_N(x)\varphi_{N-1}(x) - \varphi'_{N-1}(x)\varphi_N(x)] \tag{11b}$$

Using these identities, it is readily verified that:

  i. Equation (9) is fulfilled if the DVR points $\{x_\alpha\}$ are taken as the zeros of $\varphi_N(x)$. We then have

$$\sum_{k=0}^{N-1} \varphi_k(x_\alpha)\varphi_k(x_\beta) = \frac{k_{N-1}}{k_N}\varphi'_N(x_\alpha)\varphi_{N-1}(x_\beta)\delta_{\alpha\beta}, \tag{12}$$

so that the weights are obtained as

$$w_\alpha^{-1} = \frac{k_{N-1}}{k_N}\varphi'_N(x_\alpha)\varphi_{N-1}(x_\alpha), \tag{13}$$

  ii. The DVR basis functions $\{\Phi_\alpha(x)\}$ satisfy

$$\Phi_\alpha(x) = w_\alpha^{1/2}\sum_{k=0}^{N-1}\varphi_k(x_\alpha)\varphi_k(x) = w_\alpha^{-1/2}\frac{\varphi_N(x)}{(x-x_\alpha)\varphi'_N(x_\alpha)}, \tag{14}$$

  iii. The matrix $S_{k\alpha}$ diagonalizes the position matrix X_{kl},

$$(\mathbf{S}^\dagger\mathbf{XS})_{\alpha\beta} = (w_\alpha w_\beta)^{1/2}\int_a^b dx\, x\sum_{k=0}^{N-1}\varphi_k(x_\alpha)\varphi_k(x)\sum_{l=0}^{N-1}\varphi_l(x_\beta)\varphi_l(x) =$$

$$= (w_\alpha w_\beta)^{1/2}\left(\frac{k_{N-1}}{k_N}\right)^2\varphi_{N-1}(x_\alpha)\varphi_{N-1}(x_\beta)\int_a^b dx\, x\frac{\varphi_N^2(x)}{(x-x_\alpha)(x-x_\beta)} = x_\alpha\delta_{\alpha\beta}, \tag{15}$$

so that the eigenvalues and eigenvectors of the position matrix are nothing but the DVR points and the DVR basis functions respectively. The last equality is due to the fact that the Gaussian quadrature formula is exact for all polynomials of degree $\leq 2N-1$. As a result, we can either diagonalize the position matrix $\mathbf{X}$ in $\{\varphi_k(x)\}$, $k = 0, 1, \ldots, N-1$ or find the zeros of $\varphi_N(x)$ to obtain the DVR points, and in turn the weights from equation (13). For instance, for Hermite polynomials equation (13) gives $w_\alpha = \exp(x_\alpha^2)2^{N-1}N!\sqrt{\pi}/N^2H_{N-1}^2(x_\alpha)$.

  In the DVR basis, the matrix elements of the kinetic energy operator $T_{\alpha\beta} = \int_a^b\Phi_\alpha^*(x)\hat{T}\Phi_\beta(x)dx$ can be integrated analytically and the potential energy matrix elements are approximately diagonal and equal to the values of the potential energy function at the DVR points

$$U_{\alpha\beta} = \int_a^b\Phi_\alpha^*(x)U(x)\Phi_\beta(x)dx \cong U(x_\alpha)\delta_{\alpha\beta}. \tag{16}$$

  For illustrations, we shall now consider the sine orthonormal trigonometric basis functions.

  The orthonormal sine basis functions on the interval $[a, b]$ are defined as

$$\varphi_k(x) = \left(\frac{2}{b-a}\right)^{1/2}\sin\frac{k\pi(x-a)}{b-a}, \qquad k = 1, 2, \ldots, N. \tag{17}$$

Here equation (9) is satisfied if the DVR points are simply taken as the zeros of $\varphi_{N+1}(x)$, which are equally spaced points

$$x_\alpha = a + \frac{(b-a)\alpha}{N+1}, \qquad \alpha = 1, 2, \ldots, N. \tag{18}$$

The corresponding weights are in turn found to be all the same

$$w_\alpha = \left[\frac{2}{b-a}\sum_{k=1}^N\sin^2\frac{k\pi\alpha}{N+1}\right]^{-1} = \frac{b-a}{N+1}, \tag{19}$$

where use is made of the trigonometric identity (A.3) to obtain the last result. In this case, the kinetic energy matrix elements in the DVR basis $\{\Phi_\alpha(x)\}$, $\alpha = 1, 2, \ldots, N$ are easily calculated using identities (A.2) and (A.4). The results are

$$T_{\alpha\alpha} = \frac{\hbar^2}{2\mu}\frac{\pi^2}{2(b-a)^2}\left[\frac{2(N+1)^2+1}{3}-\frac{1}{\sin^2\alpha\pi/(N+1)}\right] \tag{20a}$$

for diagonal elements and

$$T_{\alpha\beta} = \frac{\hbar^2}{2\mu}\frac{\pi^2(-1)^{\alpha-\beta}}{2(b-a)^2}\left[\frac{1}{\sin^2(\alpha-\beta)\pi/2(N+1)}-\frac{1}{\sin^2(\alpha+\beta)\pi/2(N+1)}\right] \tag{20b}$$

for off-diagonal elements $\alpha \neq \beta$. Two limiting cases for equations (20a) and (20b) are as follows:

(i) $a \to -\infty$, $b \to \infty$, and $N \to \infty$ such that w_α remains finite we then have

$$T_{\alpha\alpha} = \frac{\hbar^2}{2\mu}\frac{\pi^2}{3w_\alpha^2}, \tag{21a}$$

$$T_{\alpha\beta} = \frac{\hbar^2}{2\mu}\frac{(-1)^{\alpha-\beta}}{w_\alpha^2}\frac{2}{(\alpha-\beta)^2}. \tag{21b}$$

(ii) $a \to 0$, $b \to \infty$, and $N \to \infty$ such that w_α remains finite, then

$$T_{\alpha\alpha} = \frac{\hbar^2}{2\mu}\frac{1}{w_\alpha^2}\left(\frac{\pi^2}{3}-\frac{1}{2\alpha^2}\right), \tag{22a}$$

$$T_{\alpha\beta} = \frac{\hbar^2}{2\mu}\frac{(-1)^{\alpha-\beta}}{w_\alpha^2}\left[\frac{2}{(\alpha-\beta)^2}-\frac{2}{(\alpha+\beta)^2}\right]. \tag{22b}$$

RESULTS AND DISCUSSION

A convenient and direct way to test the quality of the devised potential functions introduced in equations (2)—(6) for the description of the interactions in homo- and heretonuclear rare gas dimers is to calculate the vibration-rotation energy level spacings and to compare them with the available experimental results. This section is devoted to the results of such calculations.

The vibration-rotation energy levels of each rare gas dimer based on the five potential functions are obtained as the eigenvalues of the matrix of the Hamiltonian operator given in equation (7) in the DVR basis constructed from the sine basis functions in equation (17). The diagonal and off-diagonal matrix elements of the kinetic energy operator in the DVR constructed from the sine basis functions are given in equations (20a)—(20b). The matrix elements of the potential energy operator are calculated from equation (16). Depending on the size of the dimers, the dimension N of the Hamiltonian matrix being diagonalized varies between 1200—2000, and for $N \gtrsim 1200$ the asymptotic forms of the kinetic energy matrix elements in equations (21a)—(21b) may be employed in the calculations.

The vibration-rotation energy levels of a diatomic system (in $^1\Sigma$-electronic states) can be conveniently expressed as

$$E_{vJ} = \sum_{kl} Y_{kl}(v+\frac{1}{2})^k[J(J+1)]^l, \tag{23}$$

in which the coefficients Y_{kl} are calculated from the coefficients c_j in power series expansion of the diatomic potential function: $V(z) = c_0 z^2(1 + \sum_{j=1} c_j z^j)$, where $z = (R - R_e)/2$ and $2(R - R_e)/(R + R_e)$ correspond to the Dunham [26] and Ogilvie-Wang [27] expansions respectively. For both cases the analytical equations expressing the coefficients Y_{kl} in terms of the potential energy coefficients c_j have been reported. The potential expansion of Dunham diverges as $R \to \infty$, however, that of Ogilvie—Wang remains finite (within the range $-2 < z < 2$ corresponding to the entire range of internuclear distances $0 < R < \infty$) and converges faster.

The Ogilvie—Wang potential energy coefficients c_j, obtained by fitting $V(z)$ (truncated at the c_{10} term) to the discrete points from the best available empirical potential functions, were tabulated for each of the homo- and heteronuclear rare gas dimers [28]. The vibrational level spacings were subsequently calculated using equation (23) and the known relations between the coefficients Y_{kl} and the potential energy coefficients c_j along with the value of R_e [28]. The DVR vibrational spacings calcul-

T a b l e   1

Comparison of the experimental and DVR-calculated vibrational spacings $\Delta G_{v+1/2}$ (cm^{-1}) based on various potential functions for rare gas dimers

Molecules	Transition $v'' \rightarrow v'$	Experimental $\Delta G_{v+1/2}$	DVR-calculated $\Delta G_{v+1/2}$					
			Ogilvie *et al.*[†]	HFD-B [‡]	Murrell *et al.*	TT	Korona *et al.*[£]	L-J [§]
1	2	3	4	5	6	7	8	9
Ne$_2$	0-1	13.70±0.5 [a]	13.972 (13.84±0.03)		11.026	13.001	13.502 (13.46)	10.442
Ar$_2$	0-1	25.69±0.01 [b]	25.808 (25.641)	25.503 (25.58)	20.793	23.184	25.247 (25.69)	19.277
	1-2	20.58±0.02	20.759 (20.484)	20.378 (20.44)	17.638	19.463	20.506 (20.58)	16.356
	2-3	15.58±0.02	15.633 (15.546±0.012)	15.602 (15.46)	14.566	15.742	15.388 (15.58)	13.633
	3-4	10.91±0.03	10.313 (10.927±0.029)	10.691 (10.78)	11.620	12.022	10.553	11.118
	4-5	6.84±0.07	6.645 (6.743±0.061)	6.674 (6.74)	8.856	8.301	6.275	8.824
	5-6		8.626	4.001	6.350	4.580	3.921	6.763
Kr$_2$	0-1	21.56±0.54 [c]	22.008 (21.413)	21.906 (21.02)	23.707	21.471	21.098 (21.39)	21.704
	1-2	19.09±0.57	19.461 (19.271)	18.891 (18.86)	20.940	19.307	19.420 (19.25)	19.106
	2-3	16.76±0.60	17.222 (17.141)	16.705 (16.73)	18.220	17.144	16.981 (17.11)	16.642
	3-4	14.76±0.75	15.340 (15.031±0.002)	14.647 (14.62)	15.563	14.980	15.232	14.318
	4-5	12.23±0.51	12.891 (12.948±0.004)	12.235 (12.56)	12.996	12.817	12.447	12.142
	5-6	10.49±0.50	10.556 (10.904±0.004)	10.825 (10.56)	10.554	10.653	10.201	10.120
	6-7	8.92±0.44	8.372 (8.910±0.011)	8.797 (8.65)	8.276	8.490	8.734	8.258
	7-8	6.92±0.63	6.373 (6.977±0.018)	6.682 (6.86)	6.210	6.327	6.560	6.565
	8-9	5.54±0.30	4.652 (5.121±0.028)	5.268 (5.19)	4.401	4.163	5.103	5.047
Xe$_2$	0-1	19.90±0.3 [d]	20.225 (19.617)	19.025 (18.65)	20.911	19.643		21.488
	1-2	18.55±0.3	18.971 (18.419)	18.390 (17.5)	18.856	18.358		19.370
	2-3	17.20±0.3	17.436 (17.220)	17.127 (16.35)	16.845	17.092		17.343
	3-4	16.17±0.3	15.997 (16.020)	15.869 (15.2)	15.101	15.849		15.408
	4-5	14.63±0.3	14.594 (14.825)	14.003 (14.05)	14.868	14.629		13.570
	5-6	13.70±0.3	13.594 (13.634)	13.391 (12.92)	12.922	13.435		11.830
	6-7	12.63±0.3	12.537 (12.451)	12.189 (11.79)	11.004	12.271		10.194

T a b l e   1   (c o n t i n u e d)

1	2	3	4	5	6	7	8	9
	7-8	11.33±0.3	11.332 (11.278±0.001)	11.601 (10.68)	9.123	11.141		8.664
	8-9	10.15±0.3	9.210 (10.120±0.015)	10.463 (9.59)	7.297	10.045		7.244
	9-10	8.95±0.3	7.253 (8.979±0.02)	8.880 (8.52)	5.563	8.990		5.939
	10-11	7.83±0.30		7.507 (7.49)				
	11-12	6.79±0.30		6.742 (6.49)				
	12-13	5.83±0.30		(5.54)				
HeNe	0-1					2.388	2.431 (2.581*)	2.823
HeAr	0-1		5.025 (5.76±0.32)		6.779	5.375	5.151 (7.031*)	4.660
HeKr	0-1		6.894 (6.81±0.22)		7.435	6.444	7.206	7.293
HeXe	0-1		6.506 (6.96±0.27)		7.816	6.786		7.022
NeAr	0-1	18.79 ^{e}	19.557 (19.103±0.01)	18.846	16.478	19.202	18.722 (18.88)	16.588
	1-2		10.529 (10.27±0.058)	11.106	9.781	10.542	10.153 (10.34)	11.324
	2-3		2.761 (2.44±0.22)	2.316	4.781	2.552	3.630 (3.80)	3.914
NeKr	0-1	18.61 ^{f}	18.247 (18.384±0.028)	16.692	15.908	19.141	17.955 (18.32)	17.514
	1-2	11.67	11.264 (11.52±0.18)	11.090	11.661	11.209	11.821 (11.58)	12.529
	2-3	5.82	6.300 (6.81±0.64)	7.689	8.885	6.574	6.153 (5.87)	8.296
NeXe	0-1		17.412 (17.96)	16.372	15.892	17.317		17.204
	1-2		11.670 (11.916±0.032)	11.157	10.348	12.075		12.686
	2-3		6.834 (6.86±0.12)	8.080	7.049	6.594		8.781
ArKr	0-1	24.21 ^{f}	25.008 (24.112±0.001)		22.009	24.418	24.256 (24.35)	20.638
	1-2	20.49	20.319 (20.416±0.005)		19.048	20.907	20.810 (20.71)	17.853
	2-3	16.90	16.361 (16.909±0.018)		16.158	17.502	17.084 (17.15)	15.232
	3-4	13.50	13.720 (13.652±0.045)		13.365	12.981	13.124	12.785
	4-5	10.34	11.215 (10.71±0.089)		10.708	10.280	10.009	10.520
	5-6		8.835 (8.16±0.17)		8.235	8.357	8.575	8.447

T a b l e   1   (c o n t i n u e d)

1	2	3	4	5	6	7	8	9
	6-7		6.753 (6.08±0.29)			5.862	6.050	6.576
ArXe	0-1		23.678 (23.807)		25.349	23.179		21.143
	1-2		20.892 (20.650)		20.502	20.077		18.588
	2-3		18.0 (17.676±0.021)		16.015	17.062		16.167
	3-4		14.747 (14.934±0.05)		13.927	14.160		13.885
	4-5		12.382 (12.47±0.1)		11.422	12.761		11.750
	5-6		10.126 (10.35±0.19)		9.080	10.096		9.768
	6-7		8.931 (8.62±0.31)		6.935	8.841		7.946
	7-8		6.761 (7.35±0.49)		5.026	7.646		6.291
KrXe	0-1		21.161 (20.789)		22.472	21.295		23.234
	1-2		19.755 (18.957±0.002)		19.826	19.863		20.788
	2-3		17.494 (17.187±0.005)		17.257	17.064		18.451
	3-4		15.304 (15.489±0.012)		14.784	15.701		16.231
	4-5		13.185 (13.876±0.024)		13.002	14.367		14.128
	5-6		12.109 (12.359±0.042)		12.425	12.799		12.150
	6-7		10.051 (10.953±0.07)		10.204	10.574		10.299
	7-8		9.023 (9.67±0.11)		8.145	9.394		8.582
	8-9		8.229 (8.53±0.16)		6.274	8.265		7.005
	9-10		7.178 (7.54±0.23)		4.618	7.191		5.572
	10-11		6.418 (6.72±0.32)		3.199	6.178		4.290
	11-12		5.253 (6.09±0.43)		2.035	5.731		3.165

[a] Reference [29]; [b] Reference [30]; [c] Reference [31]; [d] Reference [32]; [e] Reference [33]; [f] Reference [17].
† In parentheses are Ogilvie and Wang results, reference [28].
‡ In parentheses are the calculated values from reference [6].
£ In parentheses are the calculated values from references [16, 17].
§ The well parameters D_e and R_e are all taken from reference [11].
* Reference [18].

ated using Ogilvie-Wang potential $V(z)$ are listed in the fourth column of Table 1; the values in parentheses in the same column are the corresponding vibrational spacings calculated based on equation (23). It is seen that the agreement between the two sets of spacings is quite satisfactory.

Table 1 also compares the available experimental vibrational spacings and the DVR-calculated spacings based on HFD-B (equation (2a, b)), Murrell *et al.* (equation (3a, b)), TT (equation (4a, b)), and Korona *et al.* (equation (6)) potential functions. The Eggenberger *et al.* potential (equation (5)) has been parameterized for the Ne$_2$ dimer only. Using this potential, the DVR calculation predicts two bound vibrational states for the dimer with a spacing of 12.8740 cm^{-1}, compared with the experimental value of 13.70±0.5 cm^{-1}. In addition, Table 1 includes the DVR vibrational spacings calculated for the rare gas dimers using a traditional potential function, the Lennard—Jones potential function $V(R) = D_e[(R_e/R)^{12} - (R_e/R)^6]$, in which the well parameters (depth D_e and position R_e) are all taken from [11]. Compared with the available experimental vibrational spacings, the spacings predicted by the Murrell *et al.* and Lennard—Jones potential functions are not as satisfactory as those predicted by other potentials. The Lennard—Jones potential cannot be improved further due to the lack of flexibility; however, the Murrell *et al.* potential function has several parameters that can be updated for im-

T a b l e   2

Comparison of the experimental and DVR-calculated rotational spacings ΔF_J (cm^{-1}) in the ground vibrational state of rare gas dimers based on various potential functions

Molecules	Transition $J'' \rightarrow J'$	Experimental ΔF_J	DVR-calculated ΔF_J		
			HFD-B [†]	TT	Korona *et al.* [‡]
Ar$_2$	0-1	0.115 [a]	0.119	0.118	0.118 (0.115)
	1-2	0.231	0.238	0.236	0.235 (0.231)
	2-3	0.346	0.356	0.351	0.353 (0.347)
	3-4	0.462	0.475	0.472	0.470
	0-2	0.35	0.356 (0.34)	0.354	0.352
	2-4	0.81	0.732 (0.80)	0.726	0.723
Kr$_2$	0-1	0.049 [b], 0.049 [c]	0.046	0.046	0.046 (0.050)
	1-2	0.097, 0.098	0.092	0.092	0.091 (0.097)
	2-3	0.146, 0.147	0.149	0.148	0.147 (0.146)
	3-4	0.195, 0.196	0.194	0.194	0.193
	4-5		0.241	0.240	0.239
ArKr	0-1	0.080 [d]		0.077	0.076 (0.080)
	1-2	0.160		0.154	0.153 (0.160)
	2-3	0.240		0.231	0.230 (0.240)
	3-4	0.320		0.308	0.307
NeAr	0-1	0.194 [e]	0.215	0.194	0.194 (0.194)
	1-2	0.389	0.410	0.384	0.384 (0.389)
	2-3	0.582	0.619	0.564	0.569 (0.582)
ArXe	2-3	0.193 [f]		0.194	
	3-4	0.257		0.246	
	4-5	0.321		0.323	
	5-6	0.385		0.383	
KrXe	3-4	0.147 [f]		0.144	
	4-5	0.184		0.180	
	5-6	0.221		0.214	

[a] Reference [30]; [b] Reference [17]; [c] Reference [34]; [d] Reference [35]; [e] Reference [33]; [f] Reference [36].
† In parentheses are the calculated values from reference [6].
‡ In parentheses are the calculated values from reference [17].

provement. The HFD-B and Korona *et al.* potentials that have been parameterized at a higher level of *ab initio* calculations exhibits better results.

Finally, Table 2 compares the experimental and DVR-calculated rotational spacings in the ground vibrational state of the indicated rare gas dimers for the HFD-B, TT, and Korona *et al.* potential functions. Again, the good agreement between the DVR and experimental rotational spacings is in evidence.

APPENDIX

Some useful trigonometric identities [25]

$$\sum_{k=1}^{n} \sin kx = \sin \frac{n+1}{2}x \sin \frac{nx}{2} \csc \frac{x}{2} \tag{A.1}$$

$$\sum_{k=0}^{n} \cos kx = \sin \frac{n+1}{2}x \cos \frac{nx}{2} \csc \frac{x}{2} = \frac{1}{2}\left(1 + \sin \frac{2n+1}{2}x \, / \sin \frac{x}{2}\right) \tag{A.2}$$

$$\sum_{k=1}^{n} \sin^2 kx = \frac{1}{4}[(2n+1)\sin x - \sin(2n+1)x]\csc x \tag{A.3}$$

$$\sum_{k=1}^{n} k^2 \cos kx = -\frac{\partial^2}{\partial x^2}\sum_{k=1}^{n} \cos kx. \tag{A.4}$$

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