# Potential-energy functions of diatomic molecules of the noble gases II. Unlike nuclear species

# J.F. Ogilvie and Frank Y.H. Wang

Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 10764 (Taiwan) (Received 10 September 1992)

### Abstract

By transforming the available functions of potential energy on internuclear distance of the diatomic molecules formed from two unlike atoms among He, Ne, Ar, Kr and Xe into the form V(z), we predicted the wavenumbers of both vibrational and pure rotational transitions. We compared our universal potential-energy function, developed on the basis of properties of the noble-gas diatomic species with like nuclei, with that of these heteronuclear species belonging to the same family. The values of  $R_e$  and  $c_0$  from correlations with the atomic electric polarisabilities of the atomic species according to appropriate combining relations apply to heteronuclear molecules just as well as previously to homonuclear molecules.

### Introduction

In our previous work [1] we transformed the potential-energy functions of the diatomic molecules He<sub>2</sub>, Ne<sub>2</sub>, Ar<sub>2</sub>, Kr<sub>2</sub> and Xe<sub>2</sub> of the family of noble gases from the empirical forms used to fit primarily experimental data from measurements of diverse physical properties into the form V(z) that is more directly applicable to the investigation of the spectral properties of these weakly bound species. We found a correlation between the electric dipole polarisabilities of the constituent atoms and the values of  $c_0$  (the leading coefficient in the function V(z) and  $R_{e}$  (the equilibrium internuclear distance) that we combined with either of two sets of coefficients  $c_i$ ,  $1 \le i \le 7$ , to constitute a universal representation of the potential energy for these diatomic molecules in the electronic ground state in the region below the dissociation limit; by that means we reproduced reasonably well the experimental intervals of energy between the vibrational states. For those homonuclear molecules in most cases, experimental data on the vibrational energies were available for comparison with our results; in general our predicted vibrational intervals agreed satisfactorily with the directly measured ones if not involving states too near the dissociation limit. For the diatomic molecules of the noble-gas elements containing unlike nuclei — namely HeNe, HeAr, HeKr, HeXe, NeAr, NeKr, NeXe, ArKr, ArXe and KrXe — little or no information about these spectral properties is available from experiment. Thus our predictions may aid the progress of future investigations in the laboratory.

We proceeded to transform analogously the available information on potential energy of the heteronuclear species into the form V(z). To develop a correlation of  $c_0$  and  $R_e$  with the atomic polarisabilities we had to find the proper combining

Correspondence to: Professor J.F. Ogilvie, Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 10764, Taiwan.

<sup>0022-2860/93/\$06.00 © 1993</sup> Elsevier Science Publishers B.V. All rights reserved.

rules that would reduce to the previously derived relation in the special case of the homonuclear species. On this basis we were able to predict the wavenumbers of vibrational and pure rotational transitions of these ten heteronuclear diatomic molecules. Because the nuclei are unlike, there applies no longer the prohibition of electric-dipole transitions between adjacent rotational states, or between vibration-rotational states according to the changes  $\Delta v = 1$  and  $\Delta J = \pm 1$ ; even though such transition moments are small, the enormous sensitivity of various contemporary experimental techniques may enable detection of these heteronuclear molecules in the presence of much greater concentrations of both the atoms and homonuclear molecules.

# Computational procedure and results

As previously [1], we based the treatment of the available data upon the representation of the vibration-rotational energies [2] for each electronic state of a particular isotopic species in the general form [3]

$$E_{vJ} = \sum_{k=0}^{N} \sum_{l=0}^{N} Y_{kl} (v + \frac{1}{2})^{k} [J(J+1)]^{l}$$
(1)

with as many term coefficients  $Y_{kl}$  being taken as are required to reproduce satisfactorily the available data. The coefficients  $Y_{kl}$  take into account the kinetic energy of the nuclei, the internuclear potential energy and the rotational motion of the nuclei about the centre of molecular mass. The vibrationrotational energies  $E_{vJ}$  therefore implicitly depend on the potential-energy parameters, and directly depend on the vibrational quantum number v and the quantum number J for total molecular angular momentum; the latter denotes essentially the rotational angular momentum, because these molecules have electronic ground states  $X^{1}\Sigma^{+}$  or  $0^{+}$  that lack net electronic spin or orbital angular momentum. The effects of any intrinsic nuclear angular momentum we ignore in those cases in which it is present.

The potential-energy function we express in terms of the argument  $z \equiv 2(R - R_e)/(R + R_e)$  [4],

which has the essential property of retaining finite values, specifically within the range -2 < z < 2 corresponding to the entire range of molecular existence,  $0 < R < \infty$  [5]. This radial function has the form of a truncated series in z to positive powers

$$V(z) = c_0 z^2 \left( 1 + \sum_{j=1}^{j} c_j z^j \right)$$
(2)

of form exactly analogous to that discussed by Dunham [3], which has the argument  $x \equiv (R - R_e)/R_e$ ; the latter argument bestows ill behaviour on the function V(x) as  $R \to \infty$  [5]. Both representations V(x) and V(z) are most useful in the range of internuclear distance near  $R = R_e$ , the distance at which the potential energy has a minimum value, which for the electronic ground state defines the zero of the energy scale; for the present purpose to represent the potential energy over a great range, particularly with  $R > 2R_e$  and prospectively even with  $R < \frac{1}{2}R_e$ , the utility of V(z)is paramount. The coefficients  $c_i$  of this representation are related by means of analytic expressions [6] to the spectral coefficients  $Y_{kl}$ ; in the inversion of spectral data the parameters  $c_i$  are determined iteratively through the non-linear relationships. As we determine the potential-energy function in the form V(z) by means of transformation from other functions in less useful forms (for spectral purposes), the calculation of the coefficients  $Y_{kl}$ from the previously generated parameters  $c_i$  is direct; for this purpose we use the analytic expressions reported up to  $c_{10}$  [6] and currently extended to c<sub>24</sub> [7].

According to their authors, the best available functional representations of the internuclear potential energy of the diatomic molecules of the noble gases exist in the form of analytic functions that are only piecewise continuous, for HeNe, HeAr, HeKr, HeXe [8], NeAr [9], NeKr, NeXe [10], ArKr [11], ArXe and KrXe [12] according to the indicated sources of data. For this reason we were unable to transform these data to the form V(z)directly by means of repeated analytic differentiation and subsequent exact conversion of the results into numerical values of the coefficients  $c_i$ ; we had thus recourse to effect indirectly the transformation by first generating discrete points from the functions and then fitting these points according to the method of parameter estimation of non-linear regression. Within the range  $0.65 < R/R_e < 6.5$ , the 290 points for each molecule were selected at geometrically increasing intervals of R with the incremental factor  $\delta R = 1.008$ ; by this means we ensured a good fit of both the steeply repulsive region,  $R < R_{e}$ , in which the energy varies rapidly with R up to  $\approx 100 D_{\rm c}$  (depending on the particular molecule), and the relatively slightly attractive region at large distances  $R >> R_e$ , in which the energy varies relatively slowly with R as it approaches the asymptotic value  $D_{\rm e}$ . To ensure reliable comparison with the previous results, we used the same value of the incremental factor  $\delta R$  and the same ranges of R; the fitting procedure was also the same, described in detail in ref. 1.

The values of the potential-energy coefficients  $c_i$ and other data of the molecules of diatomic noble gases having unlike nuclei appear in Table 1; the values of  $R_e$  and  $D_e$  are taken from the original sources [8-13] and are specified without associated uncertainty. Plots of the corresponding functions V(z) of HeAr, NeAr and ArKr appear in Figs. 1-3 respectively to illustrate the main features of the shapes of the curves and the numbers of vibrational states supported. Specified in Table 1, the ratio  $\sigma/D_{e}$ of the standard deviation  $\sigma$  of the fits to the equilibrium binding energies  $D_{e}$  provides a measure of the quality of the fit. According to our results, HeNe has only one bound vibrational state and thus v = 0; illustrated by means of the potentialenergy curve for HeAr in Fig. 1, the other species combining He with Ar, Kr and Xe each have two vibrational states, v = 0 and v = 1, although the latter is in each case near the dissociation limit. For the species combining Ne with Ar, Kr and Xe, the potential energy supports at least four bound vibrational states,  $0 \le v \le 3$ , illustrated by the potentialenergy curve for NeAr in Fig. 2; for clarity the vibrational states near the dissociation limit have been omitted therein. Increased numbers of vibrational states occur for the more massive molecules ArKr, ArXe and KrXe, illustrated by the curve for ArKr in Fig. 3. The intervals of energy (in wavenumber units) between adjacent vibrational states from the individual functions V(z) for potential energy according to the coefficients  $c_j$  in sets in Table 1 are presented in Table 2, and correspondingly those for adjacent rotational states within a few vibrational states in Table 3; the uncertainties attached to these values represent one standard deviation based on only the error of the potentialenergy functions arising during the fitting process. Equation (1) becomes unreliable for vibrational states near the dissociation limit, especially for relatively small values of v.

### Discussion

The coefficients of the function V(z) of each molecule in Table 1 have generally relatively small standard errors, and the magnitudes of the estimated correlation coefficients (not presented here) of the coefficients  $c_i$  derived from the matrix of variance and covariance are in almost all cases acceptably different from unity. That the coefficients are thus well defined indicates that this continuous functional form is useful over the large  $0.65R_{\rm e} \leq R \leq 6.5R_{\rm e}$ , range. of internuclear distance, as we found previously for the corresponding homonuclear diatomic molecules [1]. The standard deviations  $\sigma$  of the fits relative to the equilibrium binding energies are acceptably small (Table 1),  $\sigma/D_e < 6 \times 10^{-4}$ , for the molecules containing He, but larger for the other molecules, especially NeKr (for which the original function [10] is acknowledged to be erroneous [13]), ArXe and KrXe; the corrected parameters [13] of NeKr fail to overcome the deficiencies of the original function [10]. As our method of transformation has been demonstrated to be capable of high accuracy, indicated by the small values of  $\sigma/D_e$ , for the homonuclear molecules He<sub>2</sub>, Ne<sub>2</sub>, Ar<sub>2</sub> and Kr<sub>2</sub> previously [1] and the heteronuclear molecules containing He in the present work, the relatively large uncertainty of the functions for the specified three functions

# TABLE 1

Coefficients  $c_i$  of the potential-energy function V(z) and other properties of heteronuclear diatomic molecules of the noble gases

Property	HeNe	HeAr	HeKr	HeXe	NeAr
$c_0/m^{-1}$	55617.8	79218.9	79323.3	77204.6	192228
	$\pm 5.5$	± 7.2	± 7.2	$\pm 7.2$	+ 42
$c_1$	- 5.65337	- 5.77597	-5.80019	-5.90159	- 5.6349
-	$\pm 0.00058$	$\pm 0.00055$	$\pm 0.00055$	$\pm 0.00057$	$\pm 0.0013$
<i>c</i> <sub>2</sub>	17.0035	18.0174	18.1805	18.8950	16.2630
	$\pm 0.0031$	$\pm 0.0032$	$\pm 0.0032$	$\pm 0.0033$	+0.0072
$c_3$	- 33.2276	- 37.3654	- 37.9136	-40.4145	- 29.441
	$\pm 0.0065$	$\pm 0.0064$	$\pm 0.0064$	$\pm 0.0067$	$\pm 0.014$
<i>c</i> <sub>4</sub>	44.138	54.560	55.724	61.205	36.121
	$\pm 0.012$	$\pm 0.011$	$\pm 0.011$	$\pm 0.011$	$\pm 0.028$
C5	- 39.110	- 56.408	- 58.085	-66.162	- 32.034
5	$\pm 0.014$	$\pm 0.012$	$\pm 0.012$	$\begin{array}{c} 110 \text{AC} \\ \hline 77204.6 \\ \pm 7.2 \\ -5.90159 \\ \pm 0.00057 \\ 18.8950 \\ \pm 0.00033 \\ -40.4145 \\ \pm 0.0067 \\ 61.205 \\ \pm 0.011 \\ -66.162 \\ \pm 0.011 \\ 50.174 \\ \pm 0.035 \\ -25.703 \\ \pm 0.069 \\ 8.315 \\ \pm 0.059 \\ -1.491 \\ \pm 0.024 \\ 0.1069 \\ \pm 0.0039 \\ 3.9780 \\ 1900.8 \\ 5.3 \\ \hline \text{ArXe} \\ \hline \\ 552394 \\ \pm 309 \\ -6.1596 \\ \pm 0.0035 \\ 20.403 \\ \pm 0.021 \\ -42.043 \\ \pm 0.041 \\ 51.060 \\ \pm 0.0037 \\ -22.91 \\ \pm 0.21 \\ 46.12 \\ \pm 0.40 \\ -32.79 \\ \pm 0.34 \\ \hline \end{array}$	+0.032
C <sub>6</sub>	21.130	40.368	42.032	50.174	22.315
U U	+0.037	+ 0.034	+0.034	+0.035	+0.081
C7	- - 4.873	- 19.045	-20.166	-25.703	- 12.98
,	+0.072	+0.067	+0.066	+0.069	+ 0.16
Cs	-1.228	5.399	5.888	8.315	5.94
0	+0.062	+0.058	+0.058	+0.059	+0.14
Co	1.032	-0.748	-0.872	-1.491	- 1.761
cy	+0.025	+0.024	+0.024	+0.024	+0.056
Cia	-0.1854	0.0235	0.0375	0.1069	0.2379
- 10	+0.0041	+0.0038	+0.0038	+0.0039	+0.0091
$R_{\rm c}/10^{-10}{\rm m}$	3.0309	3.4804	3.6927	3.9780	3.4889
$D_{\rm c}/{\rm m}^{-1}$	1438.4	2010.4	1999.8	1900.8	4697.7
$\sigma/D_{\rm e}/10^{-4}$	5.3	5.1	5.1	5.3	12.5
Property	NeKr	NeXe	ArKr	ArXe	KrXe
$c_0/m^{-1}$	216338	229077	471981	552394	680831
-07	+ 181	+ 65	+ 150	+309	+ 383
<i>C</i> 1	-6.1607	-6.0753	- 5.8891	- 6.1596	-6.1570
-1	+0.0053	+0.0018	+0.0020	$\begin{array}{c} \pm 7.2 \\ -5.90159 \\ \pm 0.00057 \\ 18.8950 \\ \pm 0.0033 \\ -40.4145 \\ \pm 0.0067 \\ 61.205 \\ \pm 0.011 \\ -66.162 \\ \pm 0.011 \\ 50.174 \\ \pm 0.035 \\ -25.703 \\ \pm 0.069 \\ 8.315 \\ \pm 0.059 \\ -1.491 \\ \pm 0.024 \\ 0.1069 \\ \pm 0.0039 \\ 3.9780 \\ 1900.8 \\ 5.3 \\ \hline \\ \mathbf{ArXe} \\ \hline \\ \begin{array}{c} 552394 \\ \pm 309 \\ -6.1596 \\ \pm 0.0035 \\ 20.403 \\ \pm 0.021 \\ -42.043 \\ \pm 0.041 \\ 51.060 \\ \pm 0.069 \\ -24.408 \\ \pm 0.087 \\ -22.91 \\ \pm 0.21 \\ 46.12 \\ \pm 0.40 \\ -32.79 \\ \pm 0.34 \\ \end{array}$	+0.0036
Ca	19.855	18,965	18.380	20.403	20.407
-2	+0.030	+0.011	+0.011	+0.021	+0.021
C	- 39.031	- 35,440	- 35.644	- 42.043	-42.100
- ,	+0.059	+0.019	+0.022	+0.041	+0.041
C.	45.38	37.521	41.217	51.060	51,182
-4	+0.10	+0.036	+0.040	+ 0.069	+0.070
<i>C</i> -	- 22.83	- 12.356	- 19.514	-24.408	- 24.462
-,	+0.13	+0.047	+0.051	+0.087	+0.088
C.	-13.01	-21.80	- 15.74	- 22.91	- 23.06
~0	+0.31	+0.11	+0.12	+0.21	+0.21
C-	29.33	33.96	32.14	46.12	46.40
- /	+ 0.61	+0.20	+0.23	+0.40	+ 0.40
C.	- 20.45	-21.88	- 22.55	- 32.79	- 33.00
U	$\pm 0.52$	$\pm 0.18$	$\pm 0.20$	$\pm 0.34$	$\pm 0.34$

**NT T** 

TABLE I (continueu)	T.	ABI	LE I	(	con	tin	ued)	
---------------------	----	-----	------	---	-----	-----	------	--

Property	NeKr	NeXe	ArKr	ArXe	KrXe	
<i>c</i> 9	6.85	7.080	7.692	11.34	11.41	
	$\pm 0.21$	$\pm 0.072$	<u>+</u> 0.081	$\pm 0.14$	±0.14	
<i>c</i> <sub>10</sub>	-0.928	- 0.939	- 1.062	- 1.584	-1.595	
	$\pm 0.035$	$\pm 0.011$	± 0.013	$\pm 0.023$	$\pm 0.023$	
$R_{\rm e}/10^{-10}{\rm m}$	3.621	3.861	3.881	4.0668	4.174	
$D_{e}/m^{-1}$	4975.0	5157.5	12628	13110	16227	
$\sigma/D_{\rm e}/10^{-4}$	51.3	17.7	16.7	33.1	33.3	

above may indicate the less accurate nature of those original functions; the latter functions are in turn based on less complete and less accurately determined physical properties than for either the homonuclear molecules or the heteronuclear molecules containing He, for which measurements of the differential cross sections from scattering experiments at high resolution are available [8].

In the sense that no experimental spectral data were incorporated into the construction of the original functions for potential energy, the intervals of vibrational energy appearing in Table 2 are genuine predictions; for the same reason no comparison with experimental data is possible to allow assessment of the accuracy of the functions in the

form V(z). For most homonuclear diatomic molecules experimentally derived information about the vibrational energies was incorporated into the original functions; that the transformed functions V(z) yielded less accurately the vibrational intervals than the original functions or than the experimental data might hence indicate a deficiency in the process of transformation to generate the functions V(z). For the heteronuclear molecules, the vibrational intervals in Table 2 are probably less precise than the attached uncertainties indicate, according to experience of the prediction of such vibrational intervals of the homonuclear diatomic molecules before their functions incorporated any experimental vibrational data. Nevertheless these predicted



200000 100000 **E/m**<sup>-1</sup> 20000 10000 5000 4000 3000 2000 NeAr X  ${}^{1}\Sigma^{+}$ 1000 0 4 6 8 10  $R/10^{-10}m$ 

Fig. 1. The potential-energy function of HeAr in the ground electronic state X  ${}^{1}\Sigma^{+}$  or  $0^{+}$ ; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range  $V < 1.25D_{e}$  and logarithmic thereabove.

Fig. 2. The potential-energy function of NeAr in the ground electronic state X  ${}^{1}\Sigma^{+}$  or  $0^{+}$ ; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range  $V < 1.15D_{e}$  and logarithmic thereabove.



Fig. 3. The potential-energy function of ArKr in the ground electronic state X  ${}^{1}\Sigma^{+}$  or  $0^{+}$ ; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range  $V < 1.1D_{e}$  and logarithmic thereabove.

intervals of vibrational energy remain the best estimates available at present. For detection by means of Raman scattering, the wavenumber shifts of central Q-branches of vibration-rotational bands would correspond closely to the purely vibrational differences in Table 2. For absorption spectra (best monitored with tunable laser sources to attain the required sensitivity), the lines of maximum intensity in the P- and R-branches of the bands due to molecules in supersonic jets would be increased by several multiples of the rotational parameter (roughly half the value of the first rotational transitions in each vibrational state in Table 3) from the differences of purely vibrational energy in Table 2.

Because the pure rotational spectra of kindred essentially non-polar polyatomic species, such as  $ArCO_2$ , ArHCCH and (especially)  $ArN_2$  [14], have proved amenable to detection in emission by means of highly sensitive microwave spectroscopy with Fourier transform techniques, there exists a real possibility to detect the heteronuclear diatomic molecules of the noble gases, for which the electric dipole moments would be expected to be of the order of magnitude  $10^{-33}$  Cm. For this reason the estimates of wavenumbers of pure rotational tran-

sitions in Table 3 may assist investigators conducting such experiments. Not only does this advanced technique of microwave spectroscopy provide great sensitivity [15], but also measurements have great precision because of the lack of interference of modulation and collisional broadening [14]. Prospective measurements of these transitions in molecules from jets adiabatically expanded from nozzles to attain effective rotational temperatures < 15 Kare expected to yield much more precise frequencies than the values we provide. Indeed our values in Table 3 suffer potentially from the same sources of inaccuracy as the vibrational intervals in Table 2, namely the approximate potential-energy functions derived from various experimental data pertaining not to specific vibration-rotational states, but to some average properties. As the small rotational temperatures associated with the process of adiabatic expansion signify that only a few rotational states remain significantly populated in the limiting case and as the range of microwave frequencies currently accessible in the Fourier transform experiments extends to only about 30 GHz (or  $100 \,\mathrm{m}^{-1}$ ), the few values that we have provided should suffice for purposes of searching for transitions of a given species. Vibrational relaxation into the state v = 0 is generally less efficient during the process of adiabatic expansion than rotational relaxation; for this reason we provide rotational transitions within the vibrational states v = 1 and v = 2 in those cases in which those states exist and for which the data are likely to be relatively reliable. Because of the relatively shallow wells of potential energy exhibited by these molecules, the wavenumbers of the rotational transitions from J = 1 to J = 2 and from J = 2 to J = 3 deviate significantly from twice and thrice the wavenumber of the transition from J = 0 to J = 1 in several instances in Table 3.

Although there exist evident similarities of values among the coefficients  $c_j$  in Table 1, there are equally evident systematic trends across this table. Therefore we investigated whether a more general potential-energy function might be applicable to all fifteen molecules including like and unlike diatomic

#### TABLE 2

Predicted	intervals	of	vibrational	energies	(m <sup>-</sup>	')
-----------	-----------	----	-------------	----------	-----------------	----

Molecule	v'-v"	Interval	Molecule	v'-v"	Interval
НеАг	1-0	576 ± 32	ArXe	1-0	2380.72 ± 0.14
				2-1	$2064.97 \pm 0.68$
HeKr	1–0	$681 \pm 22$		3-2	1767.6 ± 2.1
				4-3	1493.4 ± 5.0
HeXe	1-0	$696 \pm 27$		5-4	1247 <u>+</u> 10
				6-5	$1035 \pm 19$
NeAr	1–0	$1910.3 \pm 1.0$		76	$862 \pm 31$
	2-1	$1027.2 \pm 5.8$		8–7	$735 \pm 49$
	3–2	244 ± 22			
NeKr	1–0	1838.4 ± 2.8	KrXe	1–0	2078.88 ± 0.04
	2-1	$1152 \pm 18$		2-1	$1895.76 \pm 0.20$
	3-2	681 ± 64		3-2	$1718.74 \pm 0.55$
		—		4-3	$1548.9 \pm 1.2$
NeXe	1-0	$1796.05 \pm 0.55$		5-4	$1387.6 \pm 2.4$
	2-1	$1191.6 \pm 3.2$		65	$1235.9 \pm 4.2$
	3-2	$686 \pm 12$		7-6	$1095.3 \pm 7.0$
				8-7	$967 \pm 11$
ArKr	1-0	$2411.18 \pm 0.12$		9-8	$853 \pm 16$
	2-1	$2041.57 \pm 0.58$		109	$754 \pm 23$
	3-2	$1690.9 \pm 1.8$		11-10	$672 \pm 32$
	4-3	$1365.2 \pm 4.5$		12-11	$609 \pm 43$
	5-4	$1071.0 \pm 8.9$			_
	6-5	$816 \pm 17$			
	7-6	608 + 29			

species. We generated the function

$$V(z)/D_{e} = (41.6996 \pm 0.041)z^{2}[1 - (5.5964 \pm 0.0050)z + (15.349 \pm 0.031)z^{2} - (24.683 \pm 0.082)z^{3} + (24.21 \pm 0.11)z^{4} - (14.226 \pm 0.084)z^{5} + (4.596 \pm 0.033)z^{6} - (0.6273 \pm 0.0052)z^{7}]$$
(3)

by fitting simultaneously in reduced form the potential energies in their piecewise continuous original functions of all fifteen molecules, i.e. both the ten species described in Table 1 and the five homonuclear molecules treated previously [1], within the range  $0.89 \le R/R_e \le 8.9$ ; by the reduced form we imply that both the internuclear separation and the energy were scaled, the former intrinsically within the z variable, and the latter as its ratio  $V(R)/D_e$  with the binding energy at

equilibrium. In these circumstances the leading coefficient  $c_0 = 41.6996 \pm 0.041$  is also a reduced value, and hence dimensionless; this reduced value is, as expected [15], closely equal to  $(c_1 - 1)^2$ , according to which relation  $-c_1$  would equal 5.46; the latter magnitude is indeed only slightly smaller than some fitted values of individual species in Table 1, although the magnitudes of most fitted values of  $-c_1$  are significantly larger. The function we defined [1] for only the homonuclear species is

$$V(z)/D_{\rm c} = (40.350 \pm 0.047)z^{2}[1 - (5.4656 \pm 0.0060)z + (14.662 \pm 0.037)z^{2} - (23.142 \pm 0.097)z^{3} - (22.36 \pm 0.13)z^{4} - (12.98 \pm 0.10)z^{5} + (4.153 \pm 0.039)z^{6} - (0.5625 + 0.0062)z^{7}]$$
(4)

TABLE	3
-------	---

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Molecule	v	J'-J"	Interval	Molecule	v	J'-J"	Interval
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	HeNe	0	1-0	70.6 ± 3.3	ArKr	0	1-0	8.048 ± 0.010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2-1	134.8 ± 3.9			2-1	$16.095 \pm 0.010$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$							3-2	$24.140 \pm 0.010$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	HeAr	0	1–0	$58.97 \pm 0.85$		1	1-0	$7.58 \pm 0.13$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2-1	116.70 ± 0.93			2-1	$15.16 \pm 0.13$
HeKr01-051.25 $\pm$ 0.5921-07.08 $\pm$ 0.712-1107.71 $\pm$ 0.633-221.23 $\pm$ 0.72HeXc01-044.09 $\pm$ 0.59ArXc01-06.493 $\pm$ 0.0112-187.63 $\pm$ 0.503-219.478 $\pm$ 0.0113-2129.97 $\pm$ 0.563-219.478 $\pm$ 0.011NeAr01-019.405 $\pm$ 0.0492-112.686 $\pm$ 0.0113-2129.97 $\pm$ 0.563-219.478 $\pm$ 0.013NeAr01-019.405 $\pm$ 0.0492-112.34 $\pm$ 0.153-258.133 $\pm$ 0.05321-05.83 $\pm$ 0.8211-016.1 $\pm$ 1.12-111.66 $\pm$ 0.823-232.2 $\pm$ 1.13-217.49 $\pm$ 0.823-248.2 $\pm$ 1.13-217.49 $\pm$ 0.82NeKr01-014.98 $\pm$ 0.14KrXe01-03.715 $\pm$ 0.0333-21.01.01.2361 $\pm$ 0.0293-211.166 $\pm$ 0.823-238.4 $\pm$ 3.03-210.780 $\pm$ 0.0472-125.6 $\pm$ 2.911-03.594 $\pm$ 0.0472-125.6 $\pm$ 2.92-17.187 $\pm$ 0.0483-238.4 $\pm$ 3.03-210.780 $\pm$ 0.243-237.058 $\pm$ 0.0293-210.40 $\pm$ 0.243-237.058 $\pm$ 0.0293-210.40 $\pm$ 0.243-237.058 $\pm$ 0.0293-210.40 $\pm$ 0.243-232.48 $\pm$ 0.583-232.48 $\pm$ 0.58			3–2	$171.7 \pm 1.1$			3-2	$22.74 \pm 0.14$
HeKr01-051.25 $\pm$ 0.592-114.15 $\pm$ 0.712-1107.71 $\pm$ 0.633-221.23 $\pm$ 0.72HeXc01-044.09 $\pm$ 0.59ArXc01-06.493 $\pm$ 0.0112-187.63 $\pm$ 0.502-112.686 $\pm$ 0.0113-219.97 $\pm$ 0.563-219.478 $\pm$ 0.011NeAr01-019.405 $\pm$ 0.0492-112.34 $\pm$ 0.153-218.51 $\pm$ 0.163-21016.1 $\pm$ 1.11-06.17 $\pm$ 0.153-218.51 $\pm$ 0.163-258.133 $\pm$ 0.05321-058.3 $\pm$ 0.823-217.49 $\pm$ 0.8211-016.1 $\pm$ 1.13-217.49 $\pm$ 0.823-217.49 $\pm$ 0.033-248.2 $\pm$ 1.13-217.49 $\pm$ 0.033-217.49 $\pm$ 0.033-248.2 $\pm$ 1.13-211.143 $\pm$ 0.0373-211.143 $\pm$ 0.0373-244.91 $\pm$ 0.143-211.143 $\pm$ 0.0373-234.4 $\pm$ 3.03-210.780 $\pm$ 0.0483-238.4 $\pm$ 3.03-210.780 $\pm$ 0.0483-238.4 $\pm$ 3.03-210.780 $\pm$ 0.0483-238.4 $\pm$ 3.03-210.780 $\pm$ 0.24NeXe01-012.361 $\pm$ 0.0293-211-010.84 $\pm$ 0.573-210.40 $\pm$ 0.243-237.058 $\pm$ 0.0293-210.40 $\pm$ 0.243-232.48 $\pm$ 0.583-232.48 $\pm$ 0.58						2	1-0	$7.08 \pm 0.71$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	HeKr	0	1-0	51.25 ± 0.59			2-1	$14.15 \pm 0.71$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			2-1	107.71 ± 0.63			3–2	$21.23 \pm 0.72$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			3-2	$150.43 \pm 0.72$				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	HeXe	0	1–0	44.09 ± 0.59	ArXe	Ó	1–0	6.493 ± 0.011
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2-1	$87.63 \pm 0.50$			2-1	$12.686 \pm 0.011$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			3-2	$129.97 \pm 0.56$			3–2	$19.478 \pm 0.011$
NeAr 0 1-0 19.405 $\pm$ 0.049 2-1 12.34 $\pm$ 0.15   2-1 38.792 $\pm$ 0.049 3-2 18.51 $\pm$ 0.16   3-2 58.133 $\pm$ 0.053 2 1-0 5.83 $\pm$ 0.82   1 1-0 16.1 $\pm$ 1.1 2-1 11.66 $\pm$ 0.82   2-1 32.2 $\pm$ 1.1 3-2 17.49 $\pm$ 0.82   3-2 48.2 $\pm$ 1.1 3-2 17.49 $\pm$ 0.03   NeKr 0 1-0 14.98 $\pm$ 0.14 KrXe 0 1-0 3.715 $\pm$ 0.033   2-1 29.96 $\pm$ 0.14 2-1 7.429 $\pm$ 0.037 3-2 11.143 $\pm$ 0.037   3-2 44.91 $\pm$ 0.14 3-2 11.143 $\pm$ 0.037 3-2 11.143 $\pm$ 0.037   1 1-0 12.8 $\pm$ 2.9 1 1-0 3.594 $\pm$ 0.047   2-1 25.6 $\pm$ 2.9 2-1 7.187 $\pm$ 0.048   3-2 38.4 $\pm$ 3.0 3-2 10.780 $\pm$ 0.048   3-2 10.261 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24   3-2 37.058 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24   3-2 37.058 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24						1	1-0	$6.17 \pm 0.15$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	NeAr	0	1–0	19.405 ± 0.049			2-1	$12.34 \pm 0.15$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2-1	38.792 ± 0.049			3–2	$18.51 \pm 0.16$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			3–2	$58.133 \pm 0.053$		2	1-0	$5.83 \pm 0.82$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	1-0	16.1 ± 1.1			2-1	$11.66 \pm 0.82$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			2-1	$32.2 \pm 1.1$			3-2	$17.49 \pm 0.82$
NeKr   0   1-0   14.98 $\pm$ 0.14   KrXe   0   1-0   3.715 $\pm$ 0.033     2-1   29.96 $\pm$ 0.14   2-1   7.429 $\pm$ 0.037     3-2   44.91 $\pm$ 0.14   3-2   11.143 $\pm$ 0.037     1   1-0   12.8 $\pm$ 2.9   1   1-0   3.594 $\pm$ 0.047     2-1   25.6 $\pm$ 2.9   2-1   7.187 $\pm$ 0.048   3-2   10.780 $\pm$ 0.048     3-2   38.4 $\pm$ 3.0   3-2   10.780 $\pm$ 0.048   2   1-0   3.47 $\pm$ 0.24     NeXe   0   1-0   12.361 $\pm$ 0.029   2-1   6.94 $\pm$ 0.24   3-2   10.40 $\pm$ 0.24     3-2   37.058 $\pm$ 0.029   3-2   10.40 $\pm$ 0.24   3-2   10.40 $\pm$ 0.24     3-2   32.48 $\pm$ 0.58   3-2   32.48 $\pm$ 0.58   3-2   10.40 $\pm$ 0.24			3–2	$48.2 \pm 1.1$				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	NeKr	0	10	14.98 ± 0.14	KrXe	0	1–0	$3.715 \pm 0.033$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2-1	$29.96 \pm 0.14$			2-1	$7.429 \pm 0.037$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			3–2	$44.91 \pm 0.14$			3-2	$11.143 \pm 0.037$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	1–0	$12.8 \pm 2.9$		1	1-0	$3.594 \pm 0.047$
NeXe 0 1-0 12.361 $\pm$ 0.029 2-1 6.94 $\pm$ 0.24 3-2 37.058 $\pm$ 0.029 3-2 10.780 $\pm$ 0.048 2 1-0 3.47 $\pm$ 0.24 2-1 24.715 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24 3-2 37.058 $\pm$ 0.029 1 1-0 10.84 $\pm$ 0.57 2-1 21.67 $\pm$ 0.58 3-2 32.48 $\pm$ 0.58			2-1	$25.6 \pm 2.9$			2-1	7.187 + 0.048
NeXe 0 1-0 12.361 $\pm$ 0.029 2-1 6.94 $\pm$ 0.24 2-1 24.715 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24 3-2 37.058 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24 1 1-0 10.84 $\pm$ 0.57 2-1 21.67 $\pm$ 0.58 3-2 32.48 $\pm$ 0.58			3–2	$38.4 \pm 3.0$			3-2	$10.780 \pm 0.048$
NeXe 0 1-0 12.361 $\pm$ 0.029 2-1 6.94 $\pm$ 0.24 2-1 24.715 $\pm$ 0.029 3-2 10.40 $\pm$ 0.24 3-2 37.058 $\pm$ 0.029 1 1-0 10.84 $\pm$ 0.57 2-1 21.67 $\pm$ 0.58 3-2 32.48 $\pm$ 0.58						2	1-0	$3.47 \pm 0.24$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	NeXe	0	1-0	$12.361 \pm 0.029$			2-1	$6.94 \pm 0.24$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2-1	$24.715 \pm 0.029$			3-2	10.40 + 0.24
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			3–2	37.058 + 0.029				-
$\begin{array}{ccc} 2-1 & 21.67 \pm 0.58 \\ 3-2 & 32.48 \pm 0.58 \end{array}$		1	1–0	$10.84 \pm 0.57$				
$3-2$ $32.48 \pm 0.58$			2-1	$21.67 \pm 0.58$				
			3-2	$32.48 \pm 0.58$				

Predicted intervals of rotational energies (m<sup>-1</sup>)

With the latter equation we previously used correlations of both  $R_e$  and  $D_e$  with the electric dipole polarisabilities [1] of the constituent atoms to generate a general potential-energy function applicable to the five homonuclear species in the region in which the energy is less than that at the dissociation limit. The estimated standard errors of the coefficients in eqn. (3) are slightly smaller than the corresponding quantities in eqn. (4); hence the more general function appears reasonably consistent with all the data of the 15 contributing species. In order to achieve a comparable relation for the heteronuclear diatomic molecules of the noble gases, we had to find, from the values of the electric polarisabilities  $\alpha_A$  and  $\alpha_B$  of the distinct constituent atoms A and B of the heteronuclear molecule AB, a basis of comparable correlations. To correlate with  $R_e$  we found

$$R_{\rm e}/10^{-10}\,{\rm m} = (2.097 \pm 0.043) + (2.919 \pm 0.076) \\ \times 10^{13} [\frac{1}{2} (\alpha_{\rm A} + \alpha_{\rm B})/{\rm F}\,{\rm m}^2)]^{1/3}$$
(5)

in which we used as the combining relation the



Fig. 4. The correlation between the equilibrium internuclear distance  $R_e$  of the diatomic molecules and the mean atomic electric dipole polarisability  $\alpha = \frac{1}{2}(\alpha_A + \alpha_B)$  of the molecule AB formed from atoms A and B of distinct noble gases; (**D**) experimental values, (O) values predicted according to the fitted correlation in eqn. 5.

arithmetic mean of the polarisabilities of the constituent atoms; the other derived correlation is

$$c_0/m^{-1} = (-9.75 \pm 0.52) \times 10^4 + (1.542 \pm 0.020) \\ \times 10^{32} \{ [2\alpha_A \alpha_B/(\alpha_A + \alpha_B)] / F m^2 \}^{2/3}$$
(6)

in which we used the square of the geometric mean divided by the arithmetic mean. In both cases we used all fifteen data of both the homonuclear and heteronuclear diatomic species. In the plot of the correlation of  $R_{\rm e}$  with the effective polarisability (the arithmetic mean) in Fig. 4, for clarity the points pertaining to homonuclear molecules have been omitted; the ten illustrated points can thereby be identified with the relevant molecules by reference to the values of  $R_{\rm e}$  that appear in Table 1. A plot of the correlation of  $c_0$  with the polarisability according to eqn. (6) provided a fit of comparable quality, indicated by the correlation coefficients of the fits, 0.996 and 0.999 pertaining to eqns. (5) and (6) respectively, that objectively demonstrate the results to be statistically significant. The values of the parameters in eqns. (5) and (6) agree satisfactorily with the corresponding ones previously defined [1] for the homonuclear species, the differences being within the combined uncertainties (each uncertainty stated in this article corresponds to a single estimated standard error of the relevant quantity).

By means of the general potential-energy function in either eqn. (3) or (4) combined with the predicted values of  $R_e$  and  $c_0$  according to eqns. (5) and (6), we have somewhat independent tests of the vibrational intervals in Table 2 deduced directly from the individually transformed functions V(z). In most cases the resulting predictions from eqn. (4) are rather closer to the values in Table 2 than those from eqn. (3); although the differences much exceed the nominal uncertainties associated with most values in Table 2, they are comparable to the analogous differences between the predictions from the same general potential-energy function in eqn. (4) and either the experimentally measured or individually calculated values of the homonuclear molecules [1]. As before, the transitions involving states near the dissociation limit are in worse agreement than those involving states nearer the minimum of the potential energy. In any case the agreement provides confidence that the estimates of the vibrational intervals in Table 2 are reasonably sound. The estimated wavenumbers of the rotational transitions in Table 3 are thereby also roughly confirmed.

# Conclusions

We have transformed the known potential energies of diatomic molecules having unlike nuclei of the noble gases in the electronic ground states  $X^{1}\Sigma^{+}$  or  $0^{+}$  into the common form V(z) that we related directly to properties amenable in spectral experiments, specifically the energies of the vibrational states. By this means we have achieved genuine predictions of the wavenumbers of vibrational and pure rotational transitions of these molecules for which no such experimental data have yet been recorded. Although the predicted values are undoubtedly less accurate than the estimated precisions of the values in Tables 2 and 3, they may nevertheless be useful to guide the experimental search for transitions to detect these species under conditions of adiabatic expansion from supersonic jets in absorption or Raman scattering experiments. Combined with the correlations with experimental data for  $c_0$  and  $R_e$  with atomic electric polarisabilities in eqns. (5) and (6), the potential-energy function in either eqn. (3) or (4) has utility as a universal relation applicable in the range of energy less than the dissociation limit of any diatomic molecule produced from atoms of the noble gases in their electronic ground states.

#### Acknowledgements

We thank Professor M.C.L. Gerry of the University of British Columbia for helpful discussions and the National Science Council of the Republic of China for support of this research.

### References

1 J.F. Ogilvie and F.Y.H. Wang, J. Mol. Struct., 273 (1992) 277.

- 2 J.F. Ogilvie, Spectrochim. Acta, Part A, 46 (1990) 43.
- 3 J.L. Dunham, Phys. Rev., 41 (1932) 721.
- 4 J.F. Ogilvie, Proc. R. Soc. London, Ser. A, 378 (1981) 287; 381 (1982) 479.
- 5 J.F. Ogilvie, J. Chem. Phys., 88 (1988) 2804.
- 6 J.F. Ogilvie, Comput. Phys. Commun., 30 (1983) 506.
- 7 F.M. Fernandez and J.F. Ogilvie, Phys. Rev. A, 42 (1990) 4001.
- 8 M. Keil, L.J. Danielson and P.J. Dunlop, J. Chem. Phys., 94 (1991) 296.
- 9 D.A. Barrow and R.A. Aziz, J. Chem. Phys., 89 (1988) 6189.
- 10 D.A. Barrow, M.J. Slaman and R.A. Aziz, J. Chem. Phys., 91 (1989) 6348.
- 11 R.A. Aziz and A. van Dalen, J. Chem. Phys., 78 (1983) 2413.
- 12 R.A. Aziz and A. van Dalen, J. Chem. Phys., 78 (1983) 2402.
- 13 D.A. Barrow, M.J. Slaman and R.A. Aziz, J. Chem. Phys., 96 (1992) 5555.
- 14 W. Jager and M.C.L. Gerry, Chem. Phys. Lett., 196 (1992) 274, and references cited therein.
- 15 H. Driezler, Mol. Phys., 59 (1986) 1.
- 16 R.H. Tipping and J.F. Ogilvie, J. Mol. Struct., 35 (1976) 1.