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Potential-energy functions of diatomic molecules of the noble gases
I. Like 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)

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Abstract

By transforming known potential energy-functions as a function of internuclear distance of the diatomic molecules He_2, Ne_2, Ar_2, Kr_2 and Xe_2 in their electronic ground states $X^1\Sigma_g^+$ or 0_g^+ into the form $V(z)$, we have calculated directly the vibrational energies of the corresponding bound states for comparison with experimental data. The coefficients c_j, $j > 0$, of the functions $V(z)$ are characteristic of the diatomic molecules of this family of noble gases. We derived a universal potential-energy function that employs the coefficients c_j, $j > 0$, fitted to all five species in combination with values of R_e and c_0 from correlations with the atomic electric polarisabilities; this function reproduces approximately the intervals of vibrational energy of molecules other than He_2. The possibility of a bound state of $^4He_2$ is also discussed.

INTRODUCTION

Although the non-radioactive noble gases are considered to be generally chemically inert, with only a few isolable chemical compounds known for krypton and xenon, all the atoms in this family of elements of the Periodic Table form diatomic molecules that have been detected by means of their molecular spectra. (Discrete spectra of He_2 are known for having only electronically excited states). The most physically meaningful representation of the molecular spectra of molecules containing only two nuclei with their associated electrons, which is also the most compact representation, has the form of radial functions [1], i.e. functions of which the argument is (or is based on) the internuclear separation R and which are formally independent of nuclear mass. This representation, which orig-

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Correspondence to: Dr. J.F. Ogilvie, Academia Sinica, Institute of Atomic and Molecular Sciences, P.O. Box 23-166, Taipei 10764, Taiwan. Electronic mail: ogilvie@twniams.bitnet.

inated in the classical idea that such molecules consist of two atoms, was introduced successfully into quantum mechanics, and thereby justified, first by Born and Oppenheimer [2] and later by others in more comprehensive treatments [3]. Therefore, if one seeks to predict the spectral properties of molecules, one first has to construct the potential-energy function. Of the two most common methods determine the potential-energy function of diatomic molecules, according to the spectral method we use data measured for transitions involving vibration–rotational states; by means of quantum computations one can nominally predict molecular properties that depend on the electronic distribution. Although one might apply the latter method to diatomic molecules of the noble gases, the family in the Periodic Table composed of helium, neon and so on, the implementation suffers from two difficulties: (i) the basis sets for molecular computations of these atomic species are not well developed; (ii) the weak binding of these molecules requires the interactions to be calculated with extremely great accuracy at relatively large internuclear distances. In contrast, there exists comparatively abundant information about the potential energy of pairwise interactions of (at least) like atoms of noble gases from thermodynamic, kinetic, structural and even spectral data, although the latter are relatively few and of relatively poor quality. The thermodynamic data include measurements of the molar volume under various conditions of temperature and pressure in solid, liquid and gaseous phases by means of density, permittivity and refractivity. The kinetic data include not only measurements of the diffusivity, thermal conductivity and viscosity [4] over large ranges of temperature and pressure, but also the results of scattering experiments [5] in molecular beams. The structural data are based on crystallographic measurements by X-ray and neutron diffraction, and of the liquid and gaseous phases by electron, neutron and X-ray diffraction [4], although not for all five elements in each case. The spectral data result from measurements of electronic transitions in the vacuum ultraviolet region, under conditions of poor resolution relative both to the rotational parameters that have comparatively small magnitudes and to the resolution that can be achieved in the infrared region, which is much less susceptible to the Doppler effect as a consequence of the frequency factor; attempts to measure Raman spectra of discrete transitions of these molecules have been generally unsuccessful. Owing to the diverse and numerous sources of information about the potential energy of these diatomic species, the functional forms that one customarily uses to represent this property are generally varied, and only indirectly indicate features of the vibration–rotational states by means of laborious computations.

Our objective has been to transform the best available functions from the diverse experimental and theoretical sources for the potential energy of the like atomic pairs, in order to reveal similarities in the form and details of the energies of the bound states. We have deduced a general function that, when combined with correlations based on a separate atomic property, reproduces approximately the known information about the vibrational states. Moreover, this general function may be accurate enough for many applications involving the physical properties of these elementary substances.

COMPUTATIONAL PROCEDURE AND RESULTS

We base the treatment of the available data upon the representation of the vibration–rotational energies [1] for each electronic state of a particular isotopic species in the general form [6]

$$E_{vJ} = \sum_k \sum_l Y_{kl}(v + \tfrac{1}{2})^k [J(J+1)]^l \tag{1}$$

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. We ignore the adiabatic and non-adiabatic effects to the extent that they are not contained in the effective potential-energy functions for two reasons: (i) they are expected to be small relative to the experimental error; (ii) there is, in any case, little or no information available that we could use to extend our treatment; our methods taking into account these effects in the analysis of discrete spectra are, however, well developed [7,8]. The vibration–rotational energies E_{vJ}, therefore, implicitly depend on the potential-energy parameters, 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 $X^1\Sigma_g^+$ or 0_g^+ that lack any net electronic spin or orbital angular momentum; we ignore the effects of any intrinsic nuclear angular momentum in those cases in which it is present.

We express the potential-energy function in terms of the argument $z \equiv 2(R - R_e)/(R + R_e)$ [9], which has the essential property of retaining finite values, specifically within the range $-2 < z < 2$ corresponding to the entire range of molecular existence, $0 < R < \infty$ [10]. This radial function has the form of a truncated series in z to positive powers

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

of a form exactly analogous to that discussed by Dunham [6], which has the argument $x \equiv (R - R_e)/R_e$; the latter argument bestows poor behaviour on the function $V(x)$ as $R \rightarrow \infty$ [10]. Both representations $V(x)$ and $V(z)$ are most useful in the range near $R = R_e$, the equilibrium internuclear separation at which the potential energy has a minimum value, which for the ground electronic state defines the zero of the energy scale; for the present purpose, to represent the potential energy over a great range, particularly at $R > 2R_e$ and prospectively even at $R < R_e/2$, the utilisation of $V(z)$ is paramount. The coefficients c_j of this representation are related by means of analytical expressions [11] to the spectral coefficients Y_{kl}; from spectral data the parameters c_j are determined iteratively, because of the non-linear relationships. As, in this work, 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 known parameters c_j is direct; for this purpose we use the analytic expressions previously published up to c_{10} [11] and currently extended to c_{22} [12].

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 partially continuous [13–16]. For this reason, we were unable to directly transform these data to the form $V(z)$ by means of repeated analytic differentiation and subsequent exact conversion of the results into numerical values of the coefficients c_j. We therefore had recourse to effect indirectly the transformation by generating discrete points from the functions and then fitting these points according to the method of parameter estimation by non-linear regression. Within the range $0.65 < R/R_e < 6.5$, 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 about $100\,D_e$ (depending on the particular molecule) (see Figs. 1–4), and the slightly attractive region at relatively large distances, $R \gg R_e$, in which the energy varies relatively slowly with R as it approaches the asymptotic value D_e. We selected the specified value of the incremental factor δR after numerous tests of the reproducibility of the original potential energy as a function of this factor, the range of the fit and the number of coefficients c_j. Well developed and tested over many years, the fitting program LMMI [17] that we used for this purpose provides, by means of analytic relationships for both the residuals and their partial derivatives with respect to the parameters, not only the best (i.e. most precise and unbiased) estimates of the parameters according to the criterion of the least sum of the squares of the residuals, but also their estimated standard errors and the corresponding correlation matrix. According to this procedure we sought to maintain a consistently sound statistical monitor of the significance of our results. To ensure the utmost numerical precision at all stages of the calculations, such that any inaccuracy of the final functions reflect that of the original functions rather than arising during the fitting pro-

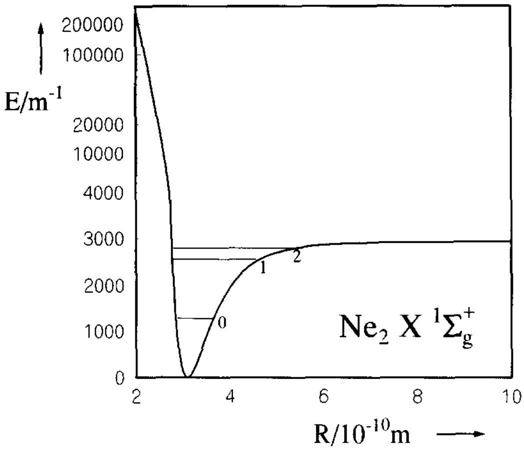

Fig. 1. The potential-energy function of Ne_2 in the ground electronic state $X^1\Sigma_g^+$ or 0_g^+; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range $V < 1.5D_e$ and logarithmic thereabove.

cedure, we have conducted all computations in Fortran with REAL*16, providing about 32 decimal digits for real numbers, and INTEGER*4 with about nine digits for integers.

The values of the potential-energy coefficients c_j and other data for the molecules in the series of diatomic noble gases having like nuclei appear in Table 1; plots of the corresponding functions $V(z)$ of Ne_2, Ar_2, Kr_2 and Xe_2 appear in Figs. 1–4; the corresponding plot for He_2 has been previously

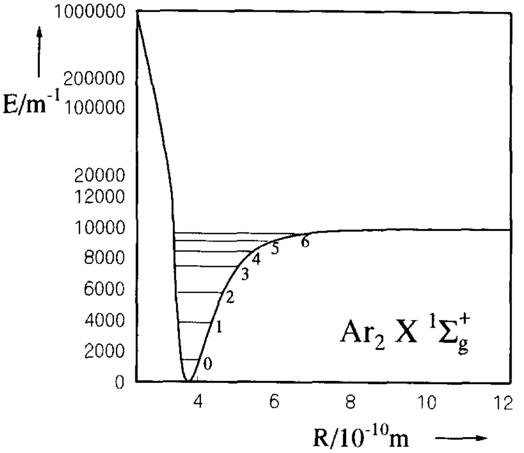

Fig. 2. The potential-energy function of Ar_2 in the ground electronic state $X^1\Sigma_g^+$ or 0_g^+; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range $V < 1.5D_e$ and logarithmic thereabove.

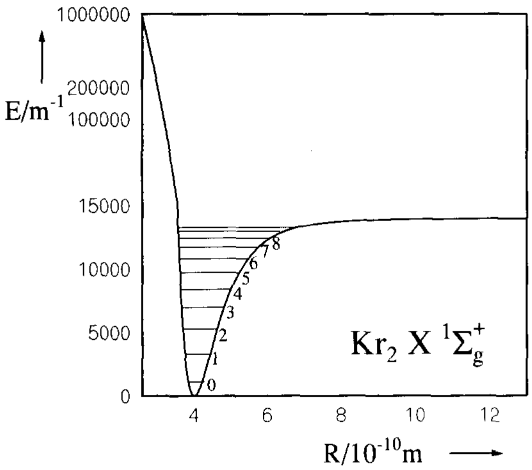

Fig. 3. The potential-energy function of Kr_2 in the ground electronic state $X^1\Sigma_g^+$ or O_g^+; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range $V < 1.5D_e$ and logarithmic thereabove.

reported [18]. We calculated the energies of the vibrational states according to known relations [11] between the term coefficients Y_{kl} and the coefficients c_j plus the value of R_e; these vibrational energies for states not too close to the dissociation limit are also depicted in Figs. 1–4. We compare the energy intervals between adjacent vibrational states from the individual functions $V(z)$ for potential energy, according to the coefficients c_j in sets

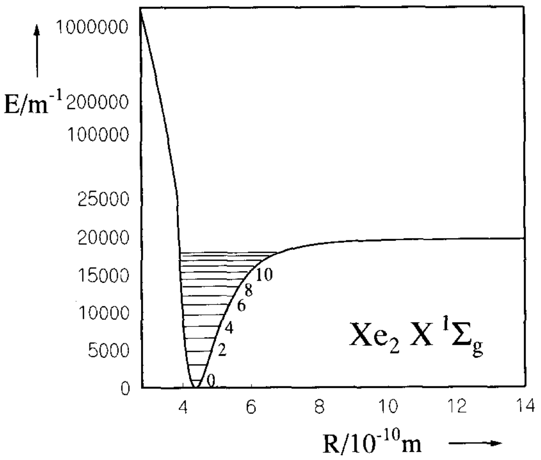

Fig. 4. The potential-energy function of Xe_2 in the ground electronic state $X^1\Sigma_g^+$ or O_g^+; the horizontal lines indicate the energies of the predicted vibrational states; the ordinate scale is linear in the range $V < 1.5D_e$ and logarithmic thereabove.

TABLE 1

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

Property	He_2	Ne_2	Ar_2	Kr_2	Xe_2
c_0 (m^{-1})	28844.2 ± 2.6	116313 ± 12	400392 ± 35	554912 ± 37	806408 ± 165
c_1	− 5.59024 ± 0.00053	− 5.80001 ± 0.00065	− 5.71692 ± 0.00052	− 5.53794 ± 0.00038	− 5.59060 ± 0.00120
c_2	16.5131 ± 0.0030	18.1942 ± 0.0037	17.1825 ± 0.0030	15.7039 ± 0.0021	15.5188 ± 0.0066
c_3	− 31.0814 ± 0.0058	− 37.8962 ± 0.0075	− 32.8913 ± 0.0057	− 27.5409 ± 0.0040	− 24.8551 ± 0.0121
c_4	38.109 ± 0.011	55.274 ± 0.014	41.404 ± 0.013	30.7522 ± 0.0100	21.128 ± 0.027
c_5	− 28.088 ± 0.014	− 56.526 ± 0.014	− 32.508 ± 0.013	− 20.292 ± 0.010	− 2.486 ± 0.036
c_6	7.793 ± 0.034	39.402 ± 0.040	12.357 ± 0.033	4.911 ± 0.025	− 14.617 ± 0.077
c_7	5.287 ± 0.066	− 17.631 ± 0.079	2.207 ± 0.064	3.429 ± 0.048	16.55 ± 0.15
c_8	− 6.118 ± 0.056	4.461 ± 0.068	− 4.493 ± 0.055	− 3.450 ± 0.041	− 8.71 ± 0.13
c_9	2.366 ± 0.023	− 0.434 ± 0.028	1.980 ± 0.022	1.210 ± 0.017	2.350 ± 0.053
c_{10}	− 0.3429 ± 0.0038	− 0.0195 ± 0.0045	− 0.2970 ± 0.0036	− 0.1610 ± 0.0028	− 0.2614 ± 0.0085
R_e (10^{-10} m)	2.9695	3.091	3.7565	4.008	4.3627
D_e (m^{-1})	762.45	2936.5	9954.5	13984.0	19620.0
σ ($D_e/10^{-4}$)	4.8	6.0	4.9	3.7	11.8

in Table 1, with experimental values [19–23] in Table 2. The uncertainties attached to the values in the second column therein represent one standard deviation based on only the error of the potential-energy functions arising during the fitting process.

TABLE 2

Comparison of experimental and calculated intervals of vibrational energies (m^{-1})

Molecule	v'–v''	Experiment	Individual[a]	General[b]
Ne_2	1–0	1370 ± 50[c]	1384 ± 3.4	1153 ± 16
Ar_2	1–0	2574 ± 5[d]	2564.06 ± 0.06	2580.2 ± 0.82
	2–1	2041 ± 5	2048.42 ± 0.34	2052.3 ± 3.6
	3–2	1561 ± 10	1554.6 ± 1.2	1514.0 ± 10
	4–3	1090 ± 10	1092.7 ± 2.9	964.0 ± 21
	5–4	678 ± 20	674.3 ± 6.1	405.0 ± 38
Kr_2	1–0	2117.5 ± 1[e]	2141.37 ± 0.007	2144.8 ± 0.2
	2–1	1909.3 ± 2	1927.14 ± 0.03	1926.4 ± 0.6
	3–2	1676 ± 60[f]	1714.10 ± 0.09	1705.5 ± 1.8
	4–3	1476 ± 75	1503.06 ± 0.20	1482.1 ± 3.3
	5–4	1223 ± 51	1294.83 ± 0.40	1256.3 ± 5.8
	6–5	1049 ± 50	1090.43 ± 0.71	1028.0 ± 9.4
	7–6	892 ± 44	891.0 ± 1.1	797.0 ± 14.0
	8–7	692 ± 63	697.7 ± 1.8	564.0 ± 20.0
	9–8	554 ± 30	512.1 ± 2.8	329.0 ± 26.0
Xe_2	1–0	1990 ± 30[g]	1961.75 ± 0.006	1968.5 ± 0.04
	2–1	1855 ± 30	1841.92 ± 0.023	1851.2 ± 0.16
	3–2	1720 ± 30	1721.98 ± 0.061	1732.9 ± 0.42
	4–3	1617 ± 30	1602.10 ± 0.13	1613.9 ± 0.58
	5–4	1463 ± 30	1482.49 ± 0.25	1494.0 ± 1.4
	6–5	1370 ± 30	1363.39 ± 0.42	1373.3 ± 2.2
	7–6	1263 ± 30	1245.06 ± 0.67	1251.7 ± 3.4
	8–7	1133 ± 30	1127.8 ± 1.0	1129.4 ± 4.8
	9–8	1015 ± 30	1012.0 ± 1.5	1006.2 ± 6.6
	10–9	895 ± 30	897.9 ± 2.0	882.3 ± 8.8

[a] These intervals of vibrational energy are calculated from the individual potential-energy functions of the respective species according to the coefficients c_j of $V(z)$ in Table 1.

[b] These intervals of vibrational energy are calculated from the universal potential-energy function in eqn. (6) in combination with the values of c_0 and R_e from the correlations in eqns. (3) and (4).

[c] Ref. 19. [d] Ref. 20. [e] Ref. 21. [f] Ref. 22. [g] Ref. 23.

DISCUSSION

The coefficients of the function $V(z)$ of each molecule He_2–Xe_2 in Table 1 have generally relatively small standard errors, and the magnitudes of the estimated correlation coefficients (not presented here) of the coefficients c_j derived from the variance–covariance matrix 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 a wide range

$0.65R_e \leqslant R \leqslant 6.5\,R_e$ of internuclear distance, as we found previously for He_2 within a somewhat more narrow range [18]. Relative to the equilibrium binding energies D_e, the standard deviations σ of the fits are acceptably small (Table 1), $< 6 \times 10^{-4}$, except for Xe_2 in which case the ratio is 1.2×10^{-3}. These relatively small magnitudes are consistent with the expectation that throughout most of the range of energies less than D_e, the potential-energy functions are as accurate as the experimental data from which the original functions were deduced. That the agreement between the measured and predicted intervals of vibrational energy in Table 2 is satisfactory is consistent with this expectation. Although the deviations between the original and our transformed potential-energy functions may be relatively larger (and even systematic) in the highly repulsive region of energies $V >> D_e$, the experimental errors in the data from which the original functions were deduced have relatively greater effects on these functions in this range. Because the original functions have been fitted well in their transformations to $V(z)$, much of the discrepancy between the experimental and predicted values of the vibrational intervals, to the extent that any discrepancy is statistically significant, reflects the inaccuracy of the original functions.

The results in Table 1 demonstrate the great similarity of the values of the coefficients c_j, $j > 0$, among the various molecules, especially the particularly characteristic coefficients c_1 and c_2, although small but significant trends are discernible even in these cases. The magnitudes of these values are greatest for Ne_2 and decrease gradually but systematically down the Periodic Table to Xe_2, as well as for He_2. Such trends in families of compounds within other columns of the Periodic Table have also been noted [24]. In contrast, the values of the corresponding coefficients c_j of other molecules, which we have determined directly from the transition frequencies of hydrides, such as LiH [7], AgH and other massive metal hydrides [25], and non-hydrides, such as SiS [26], LiCl and LiBr [8], differ greatly from those in Table 1. Hence, these values of the coefficients c_j are characteristic of molecules in this family, the diatomic noble gases having like nuclei.

Because of the evident similarities of values among the coefficients, we investigated whether a more general potential-energy function might be applicable to all five molecules. The function for Kr_2, which is slightly more accurate than the other transformed functions relative to the original functions, serves as a good approximation to any other function, provided that an appropriate value of c_0 is used; the agreement is best if the experimentally derived value of c_0 is applied for this purpose. An alternative procedure is to correlate the value of c_0 with another physical property of atoms of the noble gases. As the existence of the molecules, even if relatively weakly bound, is generally attributed to dispersion forces, the atomic

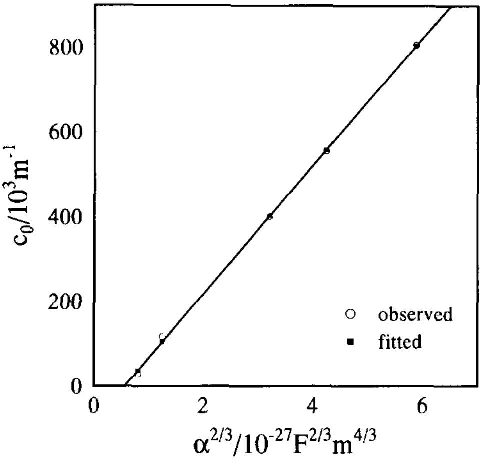

Fig. 5. Correlation between the leading potential-energy coefficient c_0 of the diatomic molecules and the atomic electric dipole polarisability α of the noble gases.

electric (dipole) polarisability seems an appropriate property. For the atomic noble-gases helium, neon, argon, krypton and xenon, these polarisabilities/10^{-40} Fm^{-2} have the values 0.2281, 0.4402, 1.8260, 2.7643 and 4.500 × 10^{-40} [27], respectively. Both the leading coefficients c_0 of the potential-energy function $V(z)$ and the equilibrium internuclear separation R_e are found to correlate well with functionals of this polarisability. For the distance R_e, the best correlation is with the cubic root of the atomic polarisability α, according to the relation

$$R_e/10^{-10}m = (2.094 \pm 0.048) + (2.9426 \pm 0.0087) \times 10^{13} (\alpha/Fm^{-2})^{1/3} \qquad (3)$$

Such a relationship is appropriate, because the atomic electric polarisability is proportional to an effective volume, which is of course related to a distance to the third power. Analogously, a relationship between the coefficient c_0 and the atomic polarisability to the power 2/3 is expected, and found

$$c_0/m^{-1} = (-8.42 \pm 0.76) \times 10^4 + (1.513 \pm 0.021) \times 10^{32} (\alpha/Fm^{-2})^{2/3} \qquad (4)$$

because the coefficient c_0 is related to the equilibrium distance r_e according to the relation $c_0 = k_e R_e^2/(hc)$. The quality of this correlation is demonstrated by the plot in Fig. 5. From these two correlations we infer a third correlation applicable to molecules in this family, namely that between c_0 and R_e; specifically

$$c_0/m^{-1} = (-6.10 \pm 0.41) \times 10^5 + (7.33 \pm 0.29) \times 10^4 (R_e/10^{-10}m)^2 \qquad (5)$$

(Although we present no plots of the other two correlations, the quality of these fits resembles that of the correlation between c_0 and α illustrated in

Fig. 5). The relatively small standard error of the second coefficient in the latter equation indicates an approximately constant force coefficient k_e at equilibrium; k_e is the curvature of the potential-energy function $V(R)$ at the minimum of the rotationless potential energy at R_e. The value of the resulting estimate $k_e \approx (2.91 \pm 0.11)\,\mathrm{N\,m^{-1}}$ is two orders smaller than that of the force coefficient $k_e = 172\,\mathrm{N\,m^{-1}}$ of I_2 (in its ground electronic state $X^1 0_g^+$), which is in turn smaller than the values commonly associated with so-called *covalent single* bonds of simple organic compounds. These magnitudes are consistent with both the relative instability, i.e. the susceptibility to dissociation, of these noble-gas molecules under typical ambient conditions and the association with essentially only dispersion effects of the slight binding that does exist. (Because of the non-negligible value of the first parameter -6.1×10^5 in the latter equation, to associate the second parameter with the force coefficient k_e is only an approximation.)

To apply to all these five diatomic species, we have deduced the following potential-energy function:

$$\begin{aligned} V(z)/D_e = {} & (40.350 \pm 0.047)z^2\,[1 - (5.4656 \pm 0.0060)z + (14.662 \pm 0.037)z^2 \\ & - (23.142 \pm 0.097)z^3 + (22.36 \pm 0.13)z^4 - (12.98 \pm 0.10)z^5 \\ & + (4.153 \pm 0.039)z^6 - (0.5625 \pm 0.0062)z^7] \end{aligned} \tag{6}$$

We generated this function by fitting simultaneously in reduced form the potential energies in their piecewise-continuous original functions [13–16] of all five molecules specified in Table 1 within the region $0.89 \leqslant R/R_e \leqslant 8.0$; 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 $c_0 = 40.350 \pm 0.047$ is also a reduced value and therefore dimensionless; as expected [28], this reduced value is in fact closely equal to $(c_1 - 1)^2$, according to which relation c_1 would equal -5.35; the latter magnitude is in fact only slightly larger than those of the individually fitted values in Table 1. We have combined this general function, excluding the value of c_0, with the values of R_e and c_0 from the correlations in eqns. (3) and (4) in order to calculate the intervals of vibrational energy; the results are given in the last column of Table 3, and the uncertainties represent the cumulative error in the fitting process and the correlations. These predicted vibrational intervals agree roughly with the experimental values as well as one could expect from such a general function. On the basis of this agreement, the latter equation constitutes an approximate universal function to describe the potential energy of any diatomic molecule of the noble gases containing like nuclei, in the region in which the potential energy is approximately equal to or less than the asymptotic value corresponding to the dissociation limit. Such an approximate universal function owes its validity to the similarities of the potential-energy functions on the individual five molecules in the form $V(z)$, as the values in Table 1 demonstrate.

As an alternative general function we combined the coefficients c_j, $1 \leqslant j \leqslant 10$, of Kr_2, presented in Table 1, again with the values of c_0 and R_e from the correlations in eqns. (3) and (4) with the atomic polarisabilities, to calculate the vibrational intervals of the diatomic molecules. The results, not given explicitly here, are generally only slightly worse than those in the final column of Table 2. In fact, the agreement is slightly better than that from the universal function, not only for Kr_2, as one might expect, but also for the higher intervals of Ar_2; however, it is significantly worse for Xe_2. We consider the function $V(z)$ in eqn. 6 the preferred form for general use. Although we attempted to extend the range of validity of this function into the strongly repulsive region of potential energy, i.e. for $R < 0.88\,R_e$, the results were unsatisfactory: the natures of the functions of the individual species differ too much in this region to permit a usefully accurate general fit, even in reduced form.

Consistent with our previous results [18], we found no bound vibrational state for He_2; as before, we expect our method not to be entirely reliable at energies very near the dissociation limit. Since those calculations were completed, Aziz and co-workers [13,29] have reported at least three further potential-energy functions for He_2. Of these, one [29] is in completely continuous analytic form although of a complicated nature, from which we deduced by repeated differentiation the following function of argument z:

$$V(z)/m^{-1} = 28979\,z^2\,(1 - 5.58413\,z + 16.3825\,z^2 - 30.5925\,z^3 + 37.416\,z^4 - 27.503\,z^5 + 6.800\,z^6 + 7.033\,z^7) \qquad (7)$$

The lack of any standard errors associated with the coefficients reflects the lack of these in the original function [29] and the fact that the transformation involved no fitting. The stated digits of the coefficients are sufficiently numerous to reproduce closely the original function in the region of R near R_e, but eqn. (7) lacks sufficient terms to approach accurately the asymptotic limit D_e, because of the complicated nature of the original function. Of the two other functions [13], the one (LM2M2) that the authors appeared to prefer is the one that we used to generate the coefficients of He_2 in Table 1. In this case the asymptotic potential energy D_e slightly exceeds the energy $E_{v=0}$ of the bound state of $^4He_2$ that Aziz et al. [30] alleged previously to exist only $0.117\,m^{-1}$ below the dissociation limit, whereas in the other case (LM2M1) [13], the purported bound state, relative to the energy zero at R_e, would lie above the dissociation limit. Even for the former function (LM2M2), the effective average internuclear distance or expectation value $\langle v = 0|R|v = 0\rangle$, for which we take the average, $8.0 \times 10^{-10}\,m$, of the classical turning points at the same energy as an inner limit, is more than three times the effective diameter, 2.2×10^{-10} m, of a helium atom according to the kinetic molecular theory of gases and measurements of thermal conductivity or viscosity [31]. To describe $^4He_2$ as having a bound vibrational state under these conditions clearly makes no sense. In contrast, in the case of Ar_2, for which, among the five species He_2–Xe_2, the vibrational energies from experiment are best determined, the gas kinetic diameter, 3.64×10^{-10} m [31], is comparable with R_e and, hence, with the expectation values of the internuclear distance in the first few vibrational states (see Fig. 2).

CONCLUSIONS

We have transformed the known potential energies of diatomic molecules having like nuclei of the noble gases in the electronic ground states $X^1\Sigma_g^+$ or 0_g^+ into the common form $V(z)$ that we related directly to spectral properties, specifically the energies of the vibrational states. We succeeded not only to reproduce satisfactorily the potential energy over a broad range of internuclear distances and intervals of vibrational energy by means of an individual function of each molecular species, but also to generate a universal potential-energy function, eqn. (6), that is approximately applicable to all the molecules He_2, Ne_2, Ar_2, Kr_2 and Xe_2 when combined with values of the coefficient c_0 and the equilibrium distance R_e from correlations, in eqns. (3) and (4), with the atomic electric polarisabilities. The coefficients $c_j, j > 0$ but especially $j = 1$ and $j = 2$, of these potential-energy functions in the form $V(z)$ are demonstrated to be characteristic of diatomic molecules in this family. For this reason we surmise that, if one were to apply eqns. (3) and (4) to estimate values of c_0 and R_e of Rn_2 from an experimental or predicted value of the atomic polarisability of radon, then one could make a useful prediction of the spectral properties of Rn_2 in its electronic ground state. According to the lists of coefficients c_j in Table 1, these functions for the individual species may be helpful for conducting future experiments on the Raman spectra of these diatomic molecules, possibly formed in a supersonic jet under conditions of adiabatic expansion.

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