

COMMENT

COMMENT REGARDING POTENTIAL FUNCTIONS, LEVEL SPACINGS
AND THERMODYNAMIC PROPERTIES OF VAN DER WAALS MOLECULES

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This comment examines and updates three recent contributions to this journal which misrepresent current knowledge of the potential energy functions, spectroscopy and thermodynamic properties of van der Waals molecules.

In the past two years, three papers [1–3] have appeared in this journal which seriously misrepresent the current state of knowledge regarding the potential energy functions and spectroscopic and other properties of van der Waals molecules. At best, their approach is obsolete, superseded by a decade of remarkable progress in both experimental techniques for studying van der Waals interactions and methods for relating characteristics of intermolecular potentials to experimental phenomena. The present comment points out some of the deficiencies of these papers and presents a more up to date picture both of our understanding of the properties of these systems and of how experimental data for them should be treated.

*(1) On the vibration–rotation spectrum of the Ne₂
van der Waals molecule*

In his recent paper on this topic, Sengupta [1] represented the Ne₂ interaction potential by a Morse function whose parameters were taken from a 1961 analysis [4] of virial coefficient data. He then used the known spectroscopic properties of a Morse potential [5] to predict the frequencies of a few lines of the far infrared ($\bar{\nu} \approx 15 \text{ cm}^{-1}$) vibration–rotation spectrum of this dimer.

In the first place, the homonuclear symmetry and spin statistics of Ne₂ make electric dipole transitions of this type strictly forbidden. In principle, transitions in this region might be observed using Raman spectroscopy, but the weak binding energies ($\lesssim 17 \text{ cm}^{-1}$) of

the bound states of this species make it difficult to form enough gas phase dimers for the Raman scattering to be observable. Of course the equilibrium population of dimers may in general be increased by lowering the temperature and raising the pressure. However, any increase in pressure substantially lowers the spectral resolution, since the weak binding energies and small level spacings of these species mean that the average lifetime of a molecule in any given quantum state is simply the time between collisions [6]. Thus, for a spectrum to be fully resolved, the pressure of the gas sample being studied must be very low. The above restrictions were encountered in the experimental studies of the Raman spectrum of Ar₂ [7] where only the envelope of the superimposed pure rotational bands for all of the populated vibrational levels was observed. This experience suggests that it would be extremely difficult to form a “Raman-observable” population of Ne₂ dimers under conditions in which individual transitions may be clearly resolved.

In contrast to the above, electronic transitions of Ne₂ in the vacuum UV region are strongly allowed, and hence are more readily observed under experimental conditions in which high spectral resolution may be obtained. Using this approach, Tanaka and Yoshino [8] observed the rotational structure of transitions originating in the $v = 0$ and 1 levels of the (van der Waals) ground electronic state. Sengupta [1] made no reference to their results or to the ensuing discussion [9–11] regarding the interpretation of these data

and their importance in determining the best potential energy curve for this system.

Another serious weakness of the discussion of ref. [1] concerns its use of a simple Morse potential proposed [4] in 1967, to represent the Ne_2 interaction. Ever since the paper of Barker and Pompe [12] in 1968, it has been clear that simple two- or three-parameter potentials such as the Morse or Lennard-Jones functions could not adequately explain all of the observed properties of the inert gas dimers. The fact that the $v = 1$ rotational constant B_1 of the Morse potential used by Sengupta [1] is more than 20% too large [8-11] is one illustration of this inadequacy.

In recent years, more realistic Ne_2 potentials have been obtained from analyses of a variety of experimental phenomena, including molecular beam scattering cross sections [13], solid-state properties such as lattice spacing, sublimation energy and compressibility [14], dilute gas bulk properties [15, 16], and from analyses based on various combinations of properties [10, 17, 18]. In an excellent summary of current knowledge of the Ne_2 interaction (in 1975), Aziz [19] critically compared the abilities of the best of the proposed potentials to accurately predict a wide range of dilute gas bulk properties, and his paper should be an essential reference in future discussions of this system.

(2) Vibrational level spacings and thermodynamic properties of inert gas van der Waals dimers

In his paper on this topic, Shin [2] described an approximate solution of the first-order WKB eigenvalue equation for a LJ (12,6) potential, which yielded a simple analytic expression for its vibrational level energies. His application of this expression to the experimental spectroscopic data [20-22] for Ar_2 , Kr_2 and Xe_2 then yielded values of the corresponding LJ (12,6) potential parameters, as well as predictions of the number and energies of all vibrational levels of these species. For Xe_2 , he then used these vibrational energies to predict values of various thermodynamic properties.

In the first place, Shin's [2] approximation of replacing the quantity $y^{7/6}$ by y in his eigenvalue equation is equivalent to replacing this LJ (12,6) potential by a Morse potential having the same depth, equilibrium distance and curvature at the minimum. His re-

sulting energy level expression is therefore precisely that for a Morse oscillator, so that all of his subsequent discussion is in fact based on use of a Morse rather than a LJ (12,6) function to represent the potential.

A serious problem with the Morse eigenvalue equation is that when parameterized to agree with the spacings of the lowest vibrational levels of these simple van der Waals molecules, it grossly underestimates the total number of bound vibrational levels. Its use in extrapolating beyond a set of experimental level energies may therefore introduce significant errors into the estimated bond dissociation energy. These tendencies were illustrated in ref. [23] where it was shown that taking proper account of the theoretically-known characteristic near-dissociation behaviour of vibrational level spacings [24, 25] showed that the Ar_2 potential well is some 7% deeper and supports 50% more vibrational levels than were predicted [20] by the linear Birge-Sponer extrapolation appropriate for a Morse potential. As a result, Shin's [2] eigenvalue expressions overlook 3 of the 9 vibrational levels of Ar_2 [23], 5 of the 16 levels of Kr_2 [21] and 7 (or 8) of the 24 (or 25) levels of Xe_2 [22]*.

Another weakness of Shin's eigenvalue equation is the fact that the values of the equilibrium distance R_e obtained on combining it with the observed vibrational spacings, are much too small. For Ar_2 , the rotational structure of the electronic spectrum reported by Colbourn and Douglas [26] showed that the correct R_e value is 9% larger than that obtained by Shin [2], while the known values for Kr_2 and Xe_2 [27] are both more than 8% larger than his estimates for these species. Indeed, even the bond lengths recommended 25 years ago by Hirschfelder et al. [28] are more accurate than those obtained by Shin [2]. The source of this difficulty appears to be the constraint, implicit in the derivation of his eigenvalue equation, that the Morse exponent parameter α be defined as $\alpha = 6/R_e$. In any case, it assures that the potentials he obtains are unlikely to provide realistic predictions of any experimental property other than the truncated sets of vibrational spacings on which they are based.

Shin's [2] use of a vibrational partition function

* Shin [2] also misinterpreted the significance of the intercept on a Birge-Sponer plot and reported a vibrational spacing for one more level than his potentials actually support for Kr_2 and Xe_2 .

generated from his (Morse) eigenvalue equation to predict values of certain thermodynamic properties of Xe_2 , is fundamentally unsound. In the first place, his neglect of higher vibrational levels (discussed above) makes his partition functions too small by 12–20% over the temperature range considered. However, a more fundamental weakness is his neglect of the effect of rotational predissociation and vibration–rotation interaction. For a chemically bound diatomic molecule, only a few of the lowest vibrational levels are populated at “normal” temperatures, and the fact that the rotational constants for these levels change fairly slowly from one level to the next means that the rotational partition function has virtually the same value for all of the populated vibrational levels. In that case, calculation of a pure vibrational contribution to various thermodynamic properties has some significance. However, the anharmonicity of the dimer potentials and the fact that *all* of their bound and quasibound levels are populated at the temperatures considered makes Shin’s predictions meaningless.

In order to generate reliable values of the internal motion partition functions of these species, two factors must be taken into account.

(i) The values of the rotational constants B_v , D_v , H_v , ... etc. change markedly over the range of populated vibrational levels; for example, the B_v constants for Ar_2 decrease by a factor of 2 over the six levels observed by Colbourn and Douglas [26], while that for the highest level $v = 8$, which is populated even at 100 K, is only ca. 5% of the value for the ground state.

(ii) Since virtually all bound or quasibound rotational levels are populated, the sum over rotational quantum number J in the partition function expression must be truncated at the value corresponding to the highest quasibound level for each v . Due to the anharmonicity of the pair potential, the value of this maximum J will decrease sharply with increasing v .

In view of the above, the only reliable way to calculate the internal motion partition functions for these weakly bound van der Waals dimers would be to perform a direct sum over all bound and quasibound vibration–rotation levels. Since rotational structure in the spectra of Kr_2 and Xe_2 has not yet been resolved [21,22] and only a fraction of the levels of Ar_2 have been observed [26], the necessary eigenvalues would have to be obtained by solution of the radial Schrödinger equation for an assumed pair potential.

However, these dimer potentials are now quite accurately known [26,27,29], and such calculations would involve a straightforward and computationally inexpensive application of standard computational methods [30].

(3) *Vibrational and thermodynamic properties of Ar–HX van der Waals molecules*

In his paper with this title, Shin [3] first assumes that eigenvalues of these systems can be reasonably approximated by the energy levels of a simple one-dimensional LJ(12,6) potential acting between the atom and the diatom. For various sets of assumed potential parameters, he then solved the first-order WKB eigenvalue equation for this potential and identified the results as energy levels of Ar–HF , Ar–HCl , Ar–HBr and Ar–HI . These eigenvalues were then used to generate corresponding vibrational partition functions and values of various thermodynamic properties for these species.

The fundamental weakness of this paper is its assumption that the eigenvalues of this type of “strong-coupling” [6,31] triatomic van der Waals complex can be realistically represented by the vibrational eigenvalues of a simple spherical potential. The relative magnitude of the stretching frequency of a diatomic halide suggests that it would be a fairly good approximation to treat this part of the complex as a rigid rotor. However, since the level spacings associated with diatom rotation are often much smaller than those associated with stretching of the van der Waals bond, effects due to internal rotation or bending cannot be ignored. The pattern of eigenvalues obtained by Dunker and Gordon [32] on performing “exact” close-coupling calculations on a variety of anisotropic Ar–HCl potential surfaces is very unlike that for a simple diatomic-like model for the complex. For example, the real ground state energy of Ar–HCl is ca. 8 cm^{-1} deeper than the lowest level of the associated spherical potential [32,33]. As a result, the vibrational spacings and thermodynamic functions which Shin [3] reported for these triatomic van der Waals molecules have little significance.

In addition to the above, the numerically-calculated LJ(12,6) eigenvalues reported by Shin [3] are unreliable. This is demonstrated by the irregular first differences between the reported vibrational spacings and by the fact that all of his potentials actually support

2–3 more vibrational levels [25,34] than were reported [3]. Moreover, his discussion repeats the error of ref. [2] in assuming that it is meaningful to consider the pure vibrational contribution to the partition functions and thermodynamic properties associated with these shallow spherical potentials.

In recent years, substantial effort has been devoted to the development of methods for calculating the eigenvalues and eigenfunctions of atom + diatom van der Waals complexes from assumed anisotropic potential energy surfaces [32,33,35–38]. As a result, it is now possible to perform reliable calculations for most levels of both weak-coupling complexes such as H_2 -Ar and strong-coupling complexes such as those discussed by Shin [3]. These methods have been used [6,33,35,39] ‡ to analyse the spectroscopic data of McKellar and Welsh [40] to obtain three-dimensional potential energy surfaces for the hydrogen–inert gas complexes. For the strong-coupling hydrogen halide–inert gas complexes, the available spectroscopic data [41] are of very high quality but are not sufficiently extensive to allow unique determination of full potential energy surfaces. Except for Ar–HCl, for which the nature of the potential surface near its minimum is fairly well known [38], the existing data for these species yield essentially only structural information. However, recently-developed techniques [42] for measuring infrared spectra of van der Waals molecules in molecular beams will hopefully begin to expand our knowledge of these species in the near future.

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‡ Although earlier than ref. [39], the best surfaces published for these systems are probably those of refs. [33].

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