

each acid changes radically upon deprotonation.

Conclusions

Ab initio calculations provide a wealth of data on the electronic structure of trisubstituted methanes and their conjugate bases. Properties of the C-H bonds poorly reflect the different origins of the substituent effects in these molecules. On the other hand, the resonance and the inductive effects can be easily distinguished by taking into account large changes in the molecular geometries, the electron densities at the critical points, and the GAPT atomic charges that occur upon deprotonation of the $\text{CH}(\text{CN})_3$ and $\text{CH}(\text{NO}_2)_3$ molecules. The observed trends are in full agreement with the expectations based on the presence of Y-aromaticity in the $\text{C}(\text{CN})_3^-$ and $\text{C}(\text{NO}_2)_3^-$ anions. The GAPT charges appear

to provide a better description of the electron density redistribution upon deprotonation than the Bader ones. The changes in molecular geometries are the probable cause of our failure to correlate the proton affinities with either the atomic charges or other molecular parameters. The unusual bonds that are found in the $\text{C}(\text{NO}_2)_3^-$ anion provide a new challenge to our understanding of chemical bonding.

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Energy-Distance Relationship in Chemical Bonding. Accurate Calculation of Potential Energy Curves

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Abstract: A function is proposed for the accurate calculation of potential energy curves of ground-state diatomics. The calculation requires knowledge of the following properties of the species: bond dissociation energy, infrared stretching frequency, equilibrium internuclear distance, electronegativity difference, effective nuclear charges, and masses. Overall, deviations between calculated and reported potentials are within a factor of 2 of the estimated uncertainties of reported RKR points. Calculated potentials are 1 order of magnitude more accurate than those obtainable with previously available methods and are consistently reliable, with no failures detected in the valence region of 50 potentials available to beyond 50% of dissociation. The calculation is applicable to polyatomic molecules.

A method is proposed for the calculation of potential energy curves describing the energy-distance relationship during the making or breaking of chemical bonds between two atoms. The accuracy obtained approaches the limits of uncertainty of available results for ground-state diatomic species. The search for a "universal" potential energy function goes back at least 60 years: Morse,¹ Rydberg,² Pöschl and Teller,³ Linnett,⁴ Frost and Musulin,⁵ Varshni,⁶ and Lippincott,⁷ among others, have attempted to formulate a universally applicable function. Such a method should be capable of accurate calculations of potential energy curves in terms of properties of reactants and products, i.e., the two separated atoms and the diatomic species formed.

The potential curve for each diatomic species can be deduced from spectroscopic measurements, involving transitions to various vibrational levels of the particular bond, through the RKR pro-

cedure.^{2,8,9} This calculation gives the energy of each vibrational level from the bottom of the potential curve and two corresponding distances or "turning points", r_{\min} and r_{\max} , for each level, thus defining the width of the curve at that energy as shown for H_2 in Figure 1. The energy is for rotational quantum number $J = 0$. The RKR procedure is a semiclassical, first-order method producing potentials within the Born-Oppenheimer approximation. Experimental results are often more accurately described by the method of inverse perturbation analysis (IPA), which is less subject to approximations associated with RKR.¹⁰ RKR and similar procedures are the only relatively direct methods available for establishing distances and corresponding energies in a "reaction coordinate", the reaction being the breaking or making of a chemical bond.

At present, no procedures exist, either semiempirical or ab initio, for the accurate calculation of potential energy curves. Desired accuracies for realistic descriptions generally are average deviations between calculated and RKR energies of less than $\pm 1\%$ of the bond dissociation energy of the species or, alternatively, of less than the "chemical" accuracy of ± 1 kcal/mol (349.74 cm^{-1} , 4.184 kJ/mol). Ab initio calculations have produced a very accurate description of the potential energy curve for the ground state of H_2 ,¹¹ but such calculations become increasingly less accurate with

(1) (a) Morse, P. M. *Phys. Rev.* **1929**, *34*, 57-64. (b) Rosen, N.; Morse, P. M. *Phys. Rev.* **1932**, 210.

(2) Rydberg, R. *Z. Phys.* **1931**, *73*, 376. *Ibid.* **1933**, *80*, 514.

(3) Pöschl, G.; Teller, E. *Z. Phys.* **1933**, *83*, 143.

(4) Linnett, J. W. *Trans. Faraday Soc.* **1940**, *36*, 1123. *Ibid.* **1942**, *38*, 1.

(5) Frost, A. A.; Musulin, B. *J. Chem. Phys.* **1954**, *22*, 1017; *J. Am. Chem. Soc.* **1954**, *76*, 2045.

(6) Varshni, Y. P. *Rev. Mod. Phys.* **1957**, *29*, 664-682.

(7) (a) Lippincott, E. R. *J. Chem. Phys.* **1953**, *21*, 2070. *Ibid.* **1955**, *23*, 603. (b) Lippincott, E. R.; Schroeder, R. *J. Chem. Phys.* **1955**, *23*, 1099. *Ibid.* **1955**, *23*, 1131; *J. Am. Chem. Soc.* **1956**, *78*, 5171; *J. Phys. Chem.* **1957**, *61*, 921. (c) Lippincott, E. R.; Dayhoff, M. O. *Spectrochim. Acta* **1960**, *16*, 807.

(d) Lippincott, E. R. *J. Chem. Phys.* **1957**, *26*, 1678. (e) Lippincott, E. R.; Steele, D.; Caldwell, P. *J. Chem. Phys.* **1961**, *35*, 123. (f) Steele, D.; Lippincott, E. R. *J. Chem. Phys.* **1961**, *35*, 2065-2075.

(8) Klein, O. *Z. Phys.* **1932**, *76*, 226.

(9) Rees, A. L. G. *Proc. Phys. Soc., London, Sect. A* **1947**, *59*, 998.

(10) Kosman, W. M.; Hinze, J. *J. Mol. Spectrosc.* **1975**, *56*, 93-103. Vidal, C. R.; Scheingraber, H. *Ibid.* **1977**, *65*, 46-64.

(11) (a) Kolos, W.; Szalewicz, K.; Monkhorst, H. J. *J. Chem. Phys.* **1986**, *84*, 3278-3283. (b) Kolos, W.; Wolniewicz, L. *J. Chem. Phys.* **1968**, *49*, 404-410. (c) *Ibid.* **1965**, *43*, 2429-2441.

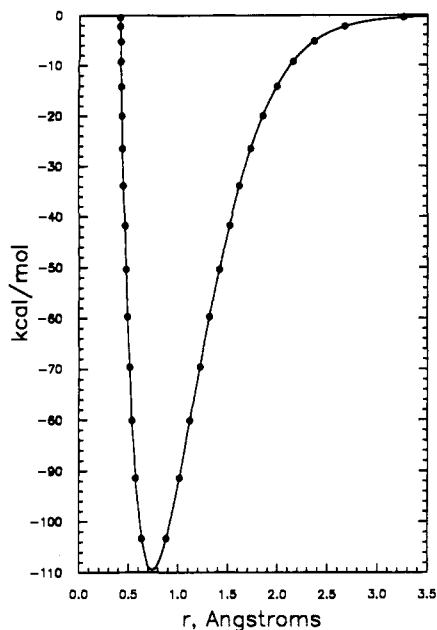


Figure 1. Energy (kcal/mol) vs distance (Å) for H₂; RKR points (ref 30). The curve is the potential calculated in this work.

heavier atoms, especially past the second row of the periodic table. Even when accurate RKR or ab initio points on the potential curve exist, it is desirable for many purposes to have an accurate analytic potential.

The usefulness and power of semiempirical potential energy functions in understanding chemical reactivity were demonstrated again recently in the use of the Morse function, modified by considerations of the empirical "bond energy-bond order" relationship.¹² Interest in transition-state modeling, either by the ab initio approach,¹³⁻¹⁵ or by other a priori semiempirical methods,¹⁶⁻¹⁸ led us to reexamine available potential energy functions. The subject has been reviewed, and the outlook for significant progress was not encouraging: "The possibility that a 'universal' potential energy curve exists can be ruled out."⁶ "It does not seem likely that any substantial improvements (errors of less than 1% of dissociation energy) can be made by suggesting new functions which have no theoretical or experimental basis. The task of giving a satisfactory theoretical or experimental foundation for any empirical function appears difficult indeed."¹⁹ "When there is a large amount of accurate experimental data of different kinds...one must tailor-make a function with a very large number of parameters to fit various parts of the curve."²⁰ As Mulliken pointed out early on,²¹ there did not seem to be any universal form for potential energy functions, each molecule having its own peculiar properties.

Earlier efforts to find universal patterns in potential energy curves were dependent on a limited number of available and reliable RKR results, generally not covering the entire potential.

Recent developments in spectroscopy have enlarged the available data base substantially, and some general patterns have been recognized.²² Having the advantage of the recently expanded data base, we were able to develop an improved function for calculating the energy-distance relationship for bond stretching (the domain $r > r_e$).²³ We now report a method for calculating potential energy curves for ground-state diatomics that is applicable to the entire distance domain and is 1 order of magnitude more accurate than the best procedure previously available. The results of the method deviate from RKR values by amounts approaching the limits of uncertainty of these values.

The proposed method should not be confused with methods that have been regarded as curve-fitting. The relative performance of such methods, including among others the extended Morse,²⁴ extended Rydberg,²⁵ and Hulburt-Hirschfelder²⁶ functions, has been reviewed.²⁴

The Function

The proposed method requires knowledge of the following properties of the ground-state diatomic species (units utilized are in parentheses): bond dissociation energy (D_e , kcal/mol, unless otherwise specified), bond length (r_e , Å), equilibrium vibrational frequency (ω_e , cm⁻¹), and the reduced mass of the diatomic species involved (μ , amu); these are also the properties required for the Morse function and for many of the other available methods. In addition, the proposed method requires the electronegativity difference ($\Delta\chi$, from Pauling's scale²⁷) and Slater's effective nuclear charges (Z).²⁸ The effect of $\Delta\chi$ on bonding led to the original formulation of Pauling's scale, and the effective nuclear charge is necessary to describe accurately the inner, repulsive part of the potential ($r < r_e$). The method does not depend on spectroscopic constants, such as anharmonicity, vibrational-rotational coupling constant, and higher terms, that cannot be deduced from limited experimental data.

Comparisons of actual RKR potentials with the standard Morse function showed the following, apparently universal, trends for ground-state diatomics: (a) Actual potentials generally rise more steeply for most of the outer limb ($r > r_e$) than the Morse function predicts. (b) The longer the equilibrium bond length, the more steep is the rise of the actual potential in the outer limb and the less steep on the inner. (c) The smaller the product of the force constant times the bond length, each normalized to D_e , the less steeply actual potentials rise on the outer limb and the reverse on the inner. (d) The greater the electronegativity difference between the two atoms, the less steep the rise on the outer limb and the reverse on the inner. (e) The smaller the product of the effective nuclear charges, the more steeply the actual potential rises on the inner limb; the effect of nuclear charges is small and indirect on the outer limb.

The above trends are described quantitatively by eqs 1-7. The potential energy function is

$$V(r) = D_e[\exp(-2\beta_{\pm}x) - 2\exp(-\beta_{\pm}x)] \quad (1)$$

where $V(r)$ denotes the bonding energy at distance r , with energy measured relative to $V(\infty) = 0$ for the separated atoms; $x = r - r_e$; β_{\pm} is a function of distance and of the properties listed above.

(12) Bürgi, H.-B.; Dunitz, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 2924-2926.

(13) For a leading reference, see: Mukherjee, D.; Wu, Y.; Fronczek, F. R.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 3329.

(14) Sherrod, M. J.; Menger, F. M. *J. Am. Chem. Soc.* **1989**, *111*, 2611-2613. This work raises some interesting questions about the conditions under which "transition-state modeling" models transition states.

(15) Saebø, S.; Beckwith, A. L. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5119-5122.

(16) Johnston, H. S.; Parr, C. *J. Am. Chem. Soc.* **1963**, *85*, 2544.

(17) Zavitsas, A. A.; Melikian, A. A. *J. Am. Chem. Soc.* **1975**, *97*, 2757-2763. Zavitsas, A. A. *J. Am. Chem. Soc.* **1972**, *94*, 2779-2879.

(18) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925-3841.

(19) Steele, D.; Lippincott, E. R.; Vanderslice, J. T. *Rev. Mod. Phys.* **1962**, *34*, 239-251.

(20) Goodisman, J. In *Diatom Interaction Potential Theory; Physical Chemistry*; Loebl, E. M., Ed.; Academic Press: New York, 1973; Vol. 31-1, p 81.

(21) Mulliken, R. S. *J. Phys. Chem.* **1937**, *41*, 5.

(22) (a) Jenc, F.; Brandt, B. A. *Phys. Rev. A* **1987**, *35*, 3784-3792. (b) *J. Chem. Phys.* **1986**, *85*, 3702-3703. (c) Jenc, F.; Brandt, B. A. *J. Chem. Phys.* **1985**, *83*, 5486-5494.

(23) Zavitsas, A. A.; Beckwith, A. L. *J. Phys. Chem.* **1989**, *93*, 5419-5426.

(24) Wright, J. S. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 219-226.

(25) Huxley, P.; Murrell, J. N. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 323-328. Murrell, J. N.; Carter, S.; Huxley, P.; Farantos, S. C.; Varandas, A. J. C. *Molecular Potential Energy Functions*; Wiley: New York, 1984.

(26) Hulburt, H. M.; Hirschfelder, J. O. *J. Chem. Phys.* **1941**, *9*, 61-69.

(27) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93. Omitted from this table is hydrogen, for which we used 2.2, the currently accepted value on this scale (Bergmann, D.; Hinze, J. In *Structure and Bonding*, Clarke, J. M., et al., Eds.; Springer-Verlag: Berlin, 1987; Vol. 66, p 152).

(28) Coulson, C. A. *Valence*; Oxford University Press: London, 1959; p 40. We calculate the effective nuclear charge for an electron approaching the atom in question, not for the highest energy electron of the atom.

The form of eq 1 is identical with that of the Morse function; Morse's "spectroscopic" constant is not a function of r and is given by

$$\beta_M = (2\pi^2 c \mu \omega^2 / h D_e)^{1/2} = 0.006513 \omega_e (\mu / D_e)^{1/2} = 8.486 (k_N)^{1/2} \quad (2)$$

where k_N denotes the equilibrium force constant ($k_e = 4\pi^2 \mu \omega^2 = (5.8923 \times 10^{-7}) \mu \omega^2$ in millidynes/angstrom), normalized to the bond dissociation energy ($k_N = k_e / D_e$).

The variable β_{\pm} of eq 1 is calculated differently for the two regions $r < r_e$ and $r > r_e$, reflecting the different nature of the predominant forces operating in the "repulsive" inner limb of the potential energy curve and the "attractive" outer limb. The dependence of β_{\pm} on r is given by a polynomial in u :

$$u = \exp(-2\beta_M x) - 2 \exp(-\beta_M x) + 1 \quad (3)$$

For $r < r_e$

$$\beta_- = \beta_M \{1 + m u^{1/2}\} \quad (4)$$

and for $r > r_e$

$$\beta_+ = \beta_M \{1 + a_1 u^{1/2} + a_2 u^n + a_3 u^{3n} + a_4 u^{5n}\} \quad (5)$$

where m and n are constants characteristic of each species and are dependent on the properties of the species:

$$m = -0.025 r_e + 0.70 \exp(-7.41 \times 10^3 k_N r_N) / (Z_1 Z_2) + 0.042 (\Delta\chi) \quad (6)$$

and

$$n = 0.70 - 0.03 r_e + 0.096 / ((1 \times 10^3) k_N r_N - 0.3) + 0.55 (\Delta\chi)^2 / r_e^{1/2} \quad (7)$$

where r_N is the normalized bond length ($r_N = r_e / D_e$). For all species, the coefficients a_i of eq 5 are given by $a_1 = -0.32m$, $a_2 = 0.15$, $a_3 = 0.2 - 0.6m$, and $a_4 = (0.21 - 3m)(\Delta\chi)^2$.

The constants of eqs 4-7 will be discussed further in the Evaluation section below, but at this point it should be noted that adequate curve-fitting procedures require at least five parameters that must be freely adjusted for each species to optimize the fitting of its RKR curve.²⁴ The proposed method has been optimized with a wide range of available ground-state potentials and describes global patterns. The resulting eqs 1-7 have no adjustable parameters; literature values of the necessary properties are used. Nothing is optimized for each case.

Results

Evaluations of the relative accuracies of different functions generally have been based on the average deviations between reported RKR energies and energies calculated by the function at the corresponding RKR turning points, as the most strict criterion. On this basis, the Lippincott function has been found^{19,20} to be superior overall among eight of the best known functions, marginally better than Varshni III.²⁹

(29) Reference 18 has misprints in the formula for the Lippincott function. See ref 23 for the correct expression.

(30) Weissman, S.; Vanderslice, J. T.; Battino, R. *J. Chem. Phys.* **1963**, *39*, 2226-2228.

(31) Krupenie, P. H.; Mason, E. A.; Vanderslice, J. T. *J. Chem. Phys.* **1963**, *39*, 2399-2401.

(32) (a) Kusch, P.; Hessel, M. M. *J. Chem. Phys.* **1977**, *67*, 586-589, RKR values for $v = 0-14$. (b) Extended to $v = 18$ by Hessel, M. M.; Vidal, C. R. *J. Chem. Phys.* **1979**, *70*, 4439-4459.

(33) Lofthus, A.; Krupenie, P. H. *J. Phys. Chem. Ref. Data* **1977**, *6*, 113-307.

(34) Krupenie, P. H. *J. Phys. Chem. Ref. Data* **1972**, *1*, 423-534.

(35) (a) Kusch, P.; Hessel, M. M. *J. Chem. Phys.* **1978**, *68*, 2591-2606, for $v = 0-45$. (b) Extended to $v = 50$ by Katô, H.; Matsui, T.; Noda, C. *J. Chem. Phys.* **1982**, *76*, 5678-5683.

Table I. Comparison of Average Deviations between Reported RKR Energies and Energies Calculated at the Reported RKR Distances

species	av dev as % of D_e			av dev this work, kcal/mol	RKR range, % dissocon	ref
	this work	Morse	Lippincott			
H ₂	0.17	5.79	5.76 ^a	0.19	99.6	30
⁷ Li ₂	0.11	3.30	1.91	0.03	53.1	31 ^b
⁷ Li ₂	0.29	4.38	2.30	0.07	65.1	32 ^c
N ₂	0.09	1.52	0.29	0.20	55.1	33
O ₂	0.85	2.07	0.83	1.02	68.1	34
Na ₂	0.60	10.15	5.86	0.10	94.9	35 ^d
⁸⁵ Rb ₂	0.64	10.94	6.89	0.07	83.9	36 ^e
I ₂	0.25	4.40	1.58	0.09	72.0	37 ^e
Cs ₂	0.72	16.04	10.01	0.08	99.3	38 ^e
⁶ LiH	0.11	2.21	2.22	0.06	74.8	39 ^e
⁷ LiH	0.31	3.97	2.91	0.18	99.4	40 ^e
OH	0.55	1.95	2.23	0.58	75.2	41
HF	0.13	4.46	5.70	0.19	99.2	42
DF	0.12	4.40	5.61	0.17	98.9	43
NaH	0.09	0.88	1.01	0.04	54.2	44,45
HCl	0.79	2.71	2.66	0.82	96.0	46
KH	0.18	2.49	2.69	0.08	99.8	47 ^f
⁸⁵ RbH	0.24	0.72	1.17	0.10	57.4	48
CsH	0.06	1.18	1.38	0.03	74.3	49
CO	0.11	0.79	3.18	0.27	69.9	50
NO	0.63	2.05	0.50	0.97	66.9	51
NaCs	0.34	10.84	6.25	0.05	93.9	52
ICl	0.25	5.70	1.19	0.13	99.7	53

^a When calculated with the unique parameters recommended for H₂ in ref 7f, this value is 3.15. ^b The value of 826.6 cm⁻¹ at $v = 2$ is a misprint; it was used as 862.6 cm⁻¹. ^c IPA. ^d Two minor errors in the reported potential were corrected according to ref 57. ^e It appears that values given above 72.7% of dissociation (above $v = 50$) may constitute an extrapolation; for the full set of reported points to $v = 82$, see Table II. ^f The innermost turning point was changed to 1.5273 Å and the outermost to 6.9934 Å, as recommended in ref 67.

Table I shows such a comparison between the performance of the method proposed here, the unabbreviated Lippincott function,¹⁹ and the Morse function as a familiar reference. The species included in Table I are ground-state diatomics selected for sat-

(36) Amiot, C.; Crozet, P.; Vergès, J. *Chem. Phys. Lett.* **1985**, *121*, 390-394.

(37) LeRoy, R. J. *J. Chem. Phys.* **1970**, *52*, 2683-2688.

(38) Weickenmeier, W.; Diemer, U.; Wahl, M.; Raab, M.; Demtröder, W.; Müller, W. *J. Chem. Phys.* **1985**, *82*, 5354-5363.

(39) Vidal, C. R. *J. Chem. Phys.* **1982**, *77*, 883-898.

(40) Chan, Y. C.; Harding, D. R.; Stwalley, W. C.; Vidal, C. R. *J. Chem. Phys.* **1986**, *85*, 2436-2444.

(41) Fallon, R. J.; Tobias, I.; Vanderslice, J. T. *J. Chem. Phys.* **1961**, *34*, 167-169.

(42) DiLorenzo, G.; Douglas, A. E. *Can. J. Phys.* **1973**, *51*, 434.

(43) Coxon, J. A.; Hajigeorgiou, P. G. *J. Mol. Spectrosc.* **1989**, *133*, 45-60.

(44) Maki, A. G.; Olson, W. B. *J. Chem. Phys.* **1989**, *90*, 6887. RKR results recommended in the critical review of ref 45.

(45) Stwalley, W. C.; Zemke, W. T.; Yang, S. C. *J. Phys. Chem. Ref. Data* **1991**, *20*, 153-187.

(46) Coxon, J. A.; Ogilvie, J. F. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1345-1362. The values reported are derived from a least-squares fit to RKR points.

(47) Hussein, K.; Effantin, C.; D'Incan, J.; Vergès, J.; Barrow, R. F. *Chem. Phys. Lett.* **1986**, *124*, 105-109. Recommended in ref 45.

(48) Katô, H.; Toyosaka, Y.; Suzuki, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 562-568. Distances were reported to three significant figures for $v = 0-15$, as may be appropriate for actual experimental significance. The values used in Table I are for the recommended potential ($v = 0-10$) from a recalculation of these results to four decimal places in ref 45.

(49) Crèpin, C.; Vergès, J.; Amiot, C. *Chem. Phys. Lett.* **1984**, *112*, 10. RKR results recommended in ref 45.

(50) Kirschner, S. M.; Watson, K. G. *J. Mol. Spectrosc.* **1974**, *51*, 321-333.

(51) Amiot, C.; Vergès, J. *J. Mol. Spectrosc.* **1980**, *81*, 424-444. Amiot, C. *J. Mol. Spectrosc.* **1982**, *94*, 150-172. An older work is in poor agreement: Vanderslice, J. T.; Mason, E. A.; Maisch, W. G. *J. Chem. Phys.* **1959**, *31*, 738-746.

(52) Diemer, U.; Weickenmeier, H.; Wahl, M.; Demtröder, W. *Chem. Phys. Lett.* **1984**, *104*, 489-495.

(53) Brand, J. C. D.; Hoy, A. R. *J. Mol. Spectrosc.* **1985**, *114*, 197-209.

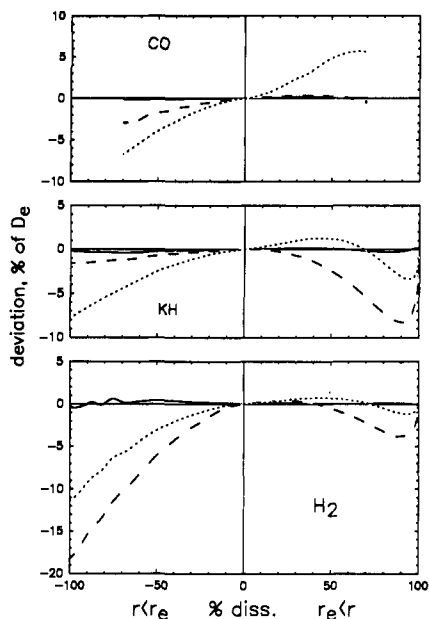


Figure 2. Deviations (% of D_e) from RKR potentials vs extent of dissociation: this work (solid line), the Lippincott function (short dashes), and the Morse function (long dashes). The percent dissociation is denoted by a minus sign for the inner limb (left panels). The horizontal line at 0 depicts RKR values: CO (ref 50), KH (ref 47), H_2 (ref 30). Negative deviations indicate that the calculated energy lies below the RKR value.

isfying the following stringent criteria: availability of RKR or IPA results for more than 50% of dissociation; availability of accurate values for the needed properties of the species; and selection by critical reviews or use in previous comparisons. For each species, Table I lists the average magnitude of the deviations between observed energies at each vibrational level and energies calculated by the three methods at the corresponding RKR or IPA distances. The average deviations are expressed as a percent of D_e , $\text{av dev} = 100 \sum |V_{\text{RKR}} - V_{\text{calcd}}| / p D_e$, where p is the number of reported points. Table I also lists the average magnitude of the deviations (kcal/mol) for this work and the percent of dissociation covered by the RKR or IPA results.

For the entries in Table I, the overall average deviation of the energies calculated by the proposed function from reported energies is $\pm 0.33\%$ of the dissociation energy of the species, 10 times superior to the Lippincott function ($\pm 3.27\%$) and 13 times superior to the Morse function ($\pm 4.47\%$). The overall average deviation (kcal/mol) of the proposed function is ± 0.24 , compared to ± 2.31 for the Morse function and ± 2.11 for the Lippincott function. The overall average extent of dissociation for all entries in Table I is 80%. The poorest agreement is found with O_2 .

The method was also used to calculate energy levels expressed in the same fashion as RKR energies, i.e., zero at the bottom of the potential well and increasing to the dissociation limit at large r , $U(\infty) = D_e$, with energies expressed in inverse centimeters. This was done in order to express energy deviations at each reported turning point as a percent of each RKR energy value. For the entries of Table I, the overall average deviation so calculated was $\pm 0.72\%$, with O_2 again providing the poorest agreement at $\pm 2.00\%$.

The curve plotted in Figure 1 for H_2 is the potential calculated by the proposed method, even though it appears to be the best fit through the RKR points. At the level of accuracy of the proposed method, deviations between RKR and calculated values are barely discernible in energy vs distance plots, such as Figure 1. Therefore, Figures 2 and 3 provide a magnification by showing deviations between RKR results and the potentials calculated by this method and the Morse and Lippincott functions. The results for CO, KH, and H_2 are shown in Figure 2; the unique parameters of the Lippincott function for H_2 were used for that species.^{7f} Figure 3 shows the results for HF and Cs_2 , where the latter is an

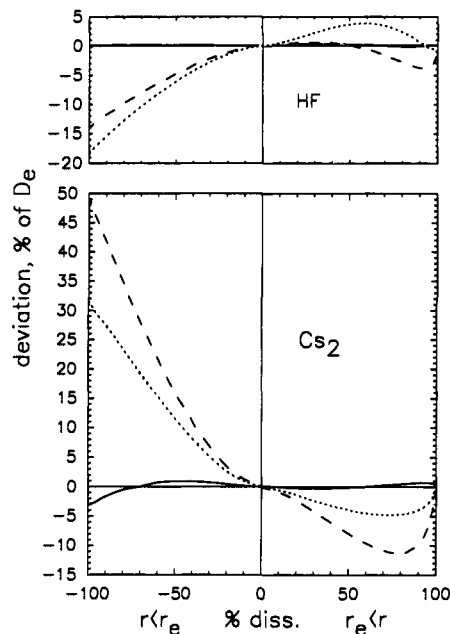


Figure 3. Deviations (% of D_e) from RKR potentials vs extent of dissociation: this work (solid line), the Lippincott function (short dashes), and the Morse function (long dashes). The percent dissociation is denoted by a minus sign for the inner limb (left panels). The horizontal line at 0 depicts RKR values: HF (ref 42) and Cs_2 (ref 38). Negative deviations indicate that the calculated energy lies below the RKR value.

Table II. Comparison of Average Deviations between Reported Potential Energies and Energies Calculated at the Corresponding r_{min} and r_{max}

species	av dev as % of D_e			av dev this work, kcal/mol	exptl ^a range, % dissocn	ref
	this work	Morse	Lippincott			
H_2	0.05	1.59	0.98 ^b	0.06	88, 100	11a ^c
$^6Li^7Li$	0.40	7.12	4.02	0.10	83, 88	55 ^d
7Li_2	0.50	7.42	3.84	0.12	90, 97	56 ^d
Na_2	0.62	7.38	4.24	0.11	66, 98	57 ^d
Na_2	0.63	9.66	5.61	0.11	88, 100	58 ^d
$^{35}Cl_2$	0.56	5.89	1.40	0.32	99, 100	59 ^d
K_2	0.71	10.37	6.47	0.09	83, 83	60 ^d
I_2	0.43	6.92	2.44	0.15	96	37 ^e
6LiH	0.29	3.64	3.38	0.17	90, 99	61 ^d
NaH	0.22	1.52	1.40	0.10	69	62 ^e
NaD	0.30	2.16	1.93	0.14	83	60 ^e
NaH	0.32	2.35	2.05	0.14	86	63 ^e
KD	0.37	0.95	0.85	0.16	62	63 ^e
^{85}RbH	0.22	0.87	1.21	0.09	66	64 ^e
^{85}RbH	0.62	1.79	1.78	0.26	78	48 ^f
CsH	0.16	1.13	1.34	0.07	68, 71	65 ^d
CsH	1.04	2.97	1.72	0.44	91, 99	66 ^d
CsH	0.12	2.17	2.19	0.05	89, 99	67 ^g
NaK	0.62	11.74	6.86	0.09	99, 99	68 ^d

^a The percent dissociation covered by rotationless potentials is given first for the inner limb, then for the outer. ^b With the unique parameters given for H_2 in ref 7f, this value is 0.63. ^c Ab initio calculation. ^d Rotationless potential. ^e RKR potential. ^f RKR potential; distances reported to three significant figures. ^g Hybrid calculation based on RKR⁴⁹ and rotationless⁶⁶ results.

example of one of the poorer agreements of the proposed method in Table I.

Table II provides additional potentials that do not meet all the stringent criteria for inclusion in Table I but are available for more than 50% of dissociation and the needed properties of the species are known fairly accurately. For example, Table I uses the recently recommended RKR potentials for the alkali hydrides, while Table II includes additional potentials for the same species, often extending to higher percentages of dissociation, even though some of them have been questioned. Table II also includes potentials of the "rotationless" type, based on rotational quantum numbers

Table III. HF. Comparative Performance of This Work and the Morse and Lippincott Functions.^a

v^b	$r, \text{\AA}^c$	$V(r), \text{RKR}$	this work	Morse	Lippincott
19	0.6220	-1.01	-1.35	-20.71	-26.79
18	0.6231	-3.01	-2.89	-21.93	-27.89
17	0.6251	-5.87	-5.66	-24.13	-29.88
16	0.6278	-9.48	-9.32	-27.04	-32.53
15	0.6310	-13.74	-13.57	-30.43	-35.61
14	0.6347	-18.57	-18.33	-34.25	-39.10
13	0.6390	-23.94	-23.70	-38.57	-43.05
12	0.6439	-29.81	-29.58	-43.34	-47.44
11	0.6494	-36.15	-35.90	-48.50	-52.20
10	0.6556	-42.94	-42.69	-54.07	-57.37
9	0.6626	-50.17	-49.93	-60.07	-62.97
8	0.6705	-57.85	-57.61	-66.48	-68.97
7	0.6795	-65.95	-65.74	-73.33	-75.43
6	0.6898	-74.50	-74.30	-80.62	-82.34
5	0.7018	-83.49	-83.33	-88.39	-89.75
4	0.7159	-92.92	-92.76	-96.62	-97.64
3	0.7331	-102.81	-102.70	-105.42	-106.13
2	0.7548	-113.17	-113.08	-114.76	-115.20
1	0.7845	-124.00	-123.95	-124.75	-124.96
0	0.8342	-135.33	-135.32	-135.48	-135.52
0	1.0206	-135.33	-135.26	-135.21	-135.13
1	1.1131	-124.00	-123.77	-123.58	-123.09
2	1.1869	-113.17	-112.81	-112.49	-111.34
3	1.2541	-102.81	-102.39	-101.98	-100.01
4	1.3181	-92.92	-92.49	-92.11	-89.22
5	1.3807	-83.49	-83.08	-82.84	-79.02
6	1.4429	-74.50	-74.14	-74.18	-69.45
7	1.5054	-65.95	-65.67	-66.12	-60.56
8	1.5688	-57.85	-57.67	-58.62	-52.36
9	1.6339	-50.17	-50.08	-51.64	-44.84
10	1.7011	-42.94	-42.96	-45.19	-38.02
11	1.7715	-36.15	-36.26	-39.19	-31.83
12	1.8460	-29.81	-29.99	-33.63	-26.28
13	1.9261	-23.94	-24.16	-28.46	-21.33
14	2.0139	-18.57	-18.77	-23.65	-16.92
15	2.1129	-13.74	-13.87	-19.16	-13.02
16	2.2286	-9.48	-9.52	-14.94	-9.60
17	2.3711	-5.87	-5.84	-10.97	-6.62
18	2.5625	-3.01	-2.95	-7.22	-4.06
19	2.8692	-1.01	-0.98	-3.68	-1.92

^aEnergies (kcal/mol) calculated at r . $V(\infty) = 0$. ^bVibrational level. ^cRKR data from ref 42. $D_e = 141.191$ kcal/mol.

greater than zero and corrected by subtraction of appropriate centrifugal terms;⁵⁴ the resulting potentials may not be reported with energy-paired values of r_{\min} and r_{\max} . Table II also includes the ab initio potential for H_2 ,^{11a} which has been considered an "exact" calculation.

The potentials used in Tables I and II are not all of the same quality. Quality judgements, however, are not appropriate in this work to avoid selecting, among several available potentials for one

- (54) Stwalley, W. C. *J. Chem. Phys.* **1972**, *56*, 2485.
 (55) Verma, K. K.; Koch, M. E.; Stwalley, W. C. *J. Mol. Spectrosc.* **1981**, *87*, 548-559.
 (56) Verma, K. K.; Koch, M. E.; Stwalley, W. C. *J. Chem. Phys.* **1983**, *78*, 3614-3622.
 (57) Verma, K. K.; Vu, T. H.; Stwalley, W. C. *J. Mol. Spectrosc.* **1981**, *85*, 131-149, Table VID. The innermost turning point ($v = 48$) is omitted; it reports an energy lower than that of $v = 47$.
 (58) Verma, K. K.; Bahns, J. T.; Rajaei-Rizi, A. R.; Stwalley, W. C.; Zemke, W. T. *J. Chem. Phys.* **1983**, *78*, 3599-3613.
 (59) Douglas, A. E.; Hoy, A. R. *Can. J. Phys.* **1975**, *53*, 1965-1975.
 (60) Ross, A. J.; Crozet, P.; d'Incan, J.; Effantin, C. *J. Phys. B* **1986**, *L145-148*.
 (61) Verma, K. K.; Stwalley, W. C. *J. Chem. Phys.* **1982**, *77*, 2350.
 (62) Zemke, W. Y.; Olson, R. E.; Verma, K. K.; Stwalley, W. C.; Liu, B. *J. Chem. Phys.* **1984**, *80*, 356; $v = 0-11$.
 (63) Giroud, M.; Nedelec, O. *J. Chem. Phys.* **1980**, *73*, 4151-4155.
 (64) Hsieh, Y. K.; Yang, S. C.; Verma, K. K.; Stwalley, W. C. *J. Mol. Spectrosc.* **1980**, *83*, 311-316.
 (65) Hsieh, Y.-K.; Yang, S.-C.; Tam, A. C.; Stwalley, W. C. *J. Chem. Phys.* **1978**, *68*, 1448-1452.
 (66) Yang, S. C. *J. Chem. Phys.* **1982**, *77*, 2884-2894.
 (67) Zemke, W. T.; Stwalley, W. C. *J. Chem. Phys. Lett.* **1988**, *143*, 84-90.
 (68) Ross, A. J.; Effantin, C.; d'Incan, J.; Barrow, R. F. *Mol. Phys.* **1985**, *56*, 903-912.

Table IV. $^{85}\text{Rb}_2$. Comparative Performance of This Work and the Morse and Lippincott Functions^a

v^b	$r, \text{\AA}^c$	$U(r), \text{IPA}$	this work	Morse	Lippincott
72	3.2039	3313	3312	4631	4179
68	3.2197	3187	3197	4429	4011
64	3.2371	3053	3073	4214	3830
60	3.2562	2911	2939	3988	3639
56	3.2770	2761	2797	3752	3438
52	3.2996	2604	2647	3508	3227
48	3.3242	2440	2488	3255	3008
44	3.3509	2269	2321	2997	2782
40	3.3800	2093	2147	2733	2549
36	3.4118	1910	1964	2464	2303
32	3.4468	1721	1774	2190	2063
28	3.4853	1527	1577	1915	1813
24	3.5283	1328	1373	1638	1559
20	3.5766	1124	1162	1361	1302
16	3.6320	914	945	1085	1044
12	3.6972	700	723	812	786
8	3.7774	481	495	543	529
4	3.8859	257	263	281	275
0	4.0960	29	29	30	29
0	4.3307	29	29	28	28
4	4.5958	257	253	238	244
8	4.7614	481	472	433	450
12	4.9010	700	687	619	670
16	5.0279	914	897	797	844
20	5.1475	1124	1104	969	1034
24	5.2629	1328	1306	1135	1219
28	5.3761	1527	1505	1296	1401
32	5.4883	1721	1698	1452	1578
36	5.6008	1910	1887	1605	1752
40	5.7145	2093	2070	1753	1921
44	5.8304	2269	2247	1899	2062
48	5.9495	2440	2419	2041	2247
52	6.0729	2604	2584	2181	2403
56	6.2016	2761	2742	2318	2554
60	6.3371	2911	2893	2453	2700
64	6.4809	3053	3036	2586	2841
68	6.6351	3187	3171	2718	2976
72	6.8022	3313	3297	2847	3104

^aEnergies (cm^{-1}) calculated at r . $U(\infty) = 3950$. ^bVibrational level. ^cIPA potential from ref 36.

species, the one fitted best by the proposed function. Isotopomers are included for this reason and to demonstrate that the calculation accounts correctly for masses, not because the method is sufficiently accurate to detect the small effects produced by breakdowns in the Born-Oppenheimer approximation, when they occur.

The entries of Table II cover an average of 88% of dissociation. The overall average deviation between calculated and reported energies is $\pm 0.43\%$ of D_e for the proposed function, compared to ± 4.6 and $\pm 2.8\%$ for the Morse and Lippincott functions, respectively. The overall average deviation (kcal/mol) of the proposed function is ± 0.15 , compared to ± 1.38 for the Morse function and ± 0.84 for the Lippincott function.

Tables III and IV show HF (RKR) and $^{85}\text{Rb}_2$ (IPA) as two specific examples of reported energy-distance results and the energies calculated at the reported values of r_{\min} and r_{\max} by the Morse and Lippincott functions and by the proposed method. The results for $^{85}\text{Rb}_2$ are presented to demonstrate one of the poorest performances of the proposed function, considerably worse than average. Table IV is presented in the RKR format. These two tables and Figure 3 also highlight the pattern of significant failures of both the Morse and Lippincott functions with species of high values of $\Delta\chi$, such as HF, or long bond lengths, such as Rb_2 and Cs_2 .

Tables I-IV and Figures 2 and 3 provide comparisons of the proposed method vs other functions; they do not provide a measure of the performance of this method vs uncertainties in the distance-energy points of the reported potentials. These uncertainties reside mainly in the r_{\min} and r_{\max} values reported, which are subject to the limitations of the RKR and similar calculations. Energies are measured accurately by spectroscopic techniques and have a negligible percent error compared to uncertainties in the reported

Table V. Average Deviations between Reported r_{\min} and r_{\max} Values and Distances Calculated in This Work at the Reported Energies^a

species	av dev, ±ppt	av dev, ±Å	range, ^b kcal/mol	range, Å ^c
H ₂	0.99	0.0011	109.49–2.21	0.413–2.675
⁷ Li ₂	0.39	0.0011	24.37–11.42	2.004–3.981
⁷ Li ₂	1.06	0.0032	24.37–7.81	1.955–4.361
N ₂	0.36	0.0004	228.43–102.58	0.887–1.559
O ₂	2.19	0.0029	120.22–38.35	0.979–1.769
Na ₂	1.64	0.0051	17.22–0.87	2.197–6.318
⁸⁵ Rb ₂	2.07	0.0099	11.29–1.82	3.204–6.802
I ₂	0.47	0.0015	35.88–10.05	2.313–3.508
Cs ₂	2.64	0.0181	10.43–0.28	3.504–9.349
⁶ LiH	0.71	0.0018	58.01–14.61	1.061–3.194
⁷ LiH	2.87	0.0098	58.01–2.02	1.010–4.290
OH	2.12	0.0026	106.60–26.39	0.702–1.760
HF	0.78	0.0012	141.19–3.22	0.623–2.563
DF	0.81	0.0013	141.30–3.13	0.624–2.560
NaH	0.37	0.0007	45.46–20.84	1.396–3.013
HCl	3.49	0.0070	106.49–4.30	0.915–2.880
KH	0.93	0.0032	42.24–1.00	1.543–5.414
⁸⁵ RbH	1.09	0.0032	41.69–17.77	1.773–3.779
CsH	0.35	0.0012	42.29–10.86	1.801–4.460
CO	0.47	0.0006	259.25–78.16	0.868–1.907
NO	1.61	0.0021	152.52–50.47	0.929–1.702
NaCs	1.21	0.0057	14.15–0.87	2.848–7.218
ICl	0.59	0.0017	50.13–1.32	1.935–4.021
H ₂	0.73	0.0011	109.49–2.38	0.423–2.646
⁶ Li ⁷ Li	1.07	0.0024	24.37–2.87	1.882–5.180
⁷ Li ₂	1.53	0.0043	24.37–0.64	1.859–6.352
Na ₂	2.14	0.0069	17.22–0.59	2.300–6.633
Na ₂	1.97	0.0068	17.22–0.37	2.225–7.027
³⁵ Cl ₂	1.90	0.0053	57.98–1.92	1.629–3.433
K ₂	1.79	0.0066	12.70–2.15	2.947–6.452
I ₂	2.59	0.0101	35.88–1.45	2.272–4.406
⁶ LiH	3.14	0.0110	58.01–1.27	1.027–4.525
NaH	0.75	0.0015	45.46–13.93	1.350–3.335
NaD	1.20	0.0022	45.46–7.51	1.314–3.739
NaH	1.21	0.0025	45.46–6.37	1.306–3.847
KD	1.59	0.0034	42.24–15.98	1.649–3.697
⁸⁵ RbH	1.07	0.0034	41.69–14.13	1.735–3.994
⁸⁵ RbH	2.01	0.0050	41.69–9.05	1.71–4.34
CsH	0.68	0.0020	42.29–12.12	1.822–4.367
CsH	3.38	0.0102	42.29–1.50	1.754–5.692
CsH	0.51	0.0017	42.29–1.56	1.754–5.692
NaK	2.09	0.0092	15.08–0.39	2.538–7.544

^aThe upper part of the table corresponds to the entries of Table I; the lower to Table II. See these tables for references. Reported values have been truncated at 98% of dissociation. ^bFrom D_e to the highest level used. For rotationless potentials, the range given pertains to the outer limb. ^cDistances from the innermost to the outermost turning point used. Values have been rounded to three decimals only for presentation in this table.

distances, which are calculated quantities. The magnitudes of these distance uncertainties are discussed below in the Evaluation section.

The “given” to which this method must be compared are the distance–energy points of RKR potentials. Standard statistical analyses to obtain estimates of “goodness of fit” of calculated values to the given points should assign the role of independent variable to the quantity with the least error in the given,⁶⁹ in this instance to energy. Comparisons of distances (at reported RKR energies as the independent variable) are not common in the literature of this field, perhaps because they are computationally more complex than comparisons of energies (at reported distances); nevertheless, they are not unprecedented.⁷⁰ Table V presents this type of comparison, i.e., of distances calculated by the proposed method vs reported r_{\min} and r_{\max} values at the same energies, implicitly assuming no error in the latter. The average magnitude of the deviations for each species is expressed as angstroms and as parts per thousand in the distance (ppt = $1000 \sum |r_{\text{RKR}} -$

$r_{\text{calcd}}/r_{\text{RKR}}|/p$); also shown are the range of energy, from D_e to the highest vibrational level used, and the distance range used. RKR values of r_{\max} are known to become increasingly unreliable near the dissociation limit on the outer limb where the energy is approaching zero asymptotically.^{22c} Irregularities, oscillations, or “ripples” often appear on the upper part of the steep inner limb,^{71,72} and r_{\min} distances are often “shifted” to provide monotonic behavior.^{56,66} For these reasons, reported potentials were truncated at 98% of dissociation for the calculations of Table V.

The first part of Table V corresponds to the entries in Table I and the second to those of Table II. The overall average deviation between calculated and reported r_{\min} and r_{\max} values is ± 1.27 ppt for the first part of the table and ± 1.65 for the second. These deviations are of the same order of magnitude as the uncertainties of reported r_{\min} and r_{\max} values (see Evaluation section).

Table VI shows specific examples of comparisons between reported r_{\min} and r_{\max} values and distances calculated by the proposed method at the same energy values. The table includes one of the rotationless potentials for CsH,⁶⁶ as an example of one of the largest average deviations found in Tables I, II, and V, along with the recommended,⁴⁵ but more limited, RKR potential for CsH. KH illustrates about average performance (see also Figure 2), while Na₂ is somewhat worse than average. The values for H₂ can be compared with Figures 1 and 2.

In addition to those included in Tables I and II, other RKR potentials are available that have been superseded by more recent work, and the proposed method was tested against some of them with no evidence of failure, as follows (values in parentheses represent average deviation in energy as percent of D_e and extent of dissociation covered by the RKR results): ⁷Li₂ (± 0.17 , 53.1%);^{32a} O₂ (± 0.74 , 68.1%);⁷¹ ³⁵Cl₂ (± 0.12 , 39.5%);⁷³ I₂ (± 2.31 , 96.0%);⁷⁴ HF (± 0.43 , 97.7%) and DF (± 0.55 , 94.7%);⁷⁵ and KH (± 0.18 , 72.3%).⁶³

Many other potentials have been reported but do not satisfy the criteria for inclusion in Tables I, II, and V, because either some needed property is not known accurately or the reported extent of dissociation is less than 50%, or both. The proposed method was tested against the following with no obvious evidence of failure: BH (available extent of dissociation 28%),⁷⁶ CN (51%),⁷⁷ PH (48%),⁷⁸ BO (43%),⁷⁹ SiO (55%),⁸⁰ BaO (50%),⁸¹ PO (20%),⁸² Br₂ (21%),⁸³ Bi₂ (46%),⁸⁴ BrCl (18%),⁸⁵ etc. However, good agreement with potentials not known to high extents of dissociation is not very meaningful since all Morse-type functions perform well near the bottom of the potential curve. For some of the above species, there are large uncertainties in D_e or r_e and, therefore, poorer agreement is also not meaningful. E.g., for PO and BaO, the bond strength is reported⁸⁶ with uncertainties of ± 3.5 kcal/mol (± 1220 cm⁻¹) and ± 2 kcal/mol (± 670 cm⁻¹), respectively; for CN, recommended values of D_0 vary from 178.1⁸⁶ to 185.1⁸⁷ kcal/mol and values of r_e range from 1.175⁸⁶ to 1.171

(71) Vanderslice, J. T.; Mason, E. A.; Maisch, W. G. *J. Chem. Phys.* **1960**, *32*, 515–522. This appears to be the first observation of this problem.

(72) Wells, B. H.; Smith, E. B.; Zare, R. N. *Chem. Phys. Lett.* **1983**, *99*, 244–249.

(73) Coxon, J. A. *J. Mol. Spectrosc.* **1980**, *82*, 264–282.

(74) Verma, R. D. *J. Chem. Phys.* **1960**, *32*, 738–749.

(75) Fallon, R. J.; Vanderslice, J. T.; Mason, E. A. *J. Chem. Phys.* **1960**, *32*, 698–700.

(76) Pianalto, F. S.; O'Brien, L. C.; Keller, P. C.; Bernath, P. F. *J. Mol. Spectrosc.* **1988**, *129*, 348–353.

(77) Fallon, R. D.; Vanderslice, J. T.; Cloney, R. D. *J. Chem. Phys.* **1962**, *37*, 1097–1100.

(78) Ram, S.; Bernath, P. F. *J. Mol. Spectrosc.* **1987**, *122*, 275–281.

(79) Coxon, J. A.; Foster, S. C.; Naxakis, S. J. *Mol. Spectrosc.* **1984**, *105*, 465–479.

(80) Tipping, R. H.; Chackerian, C., Jr. *J. Mol. Spectrosc.* **1981**, *88*, 352–363.

(81) Field, R. W.; Capelle, G. A.; Revelli, M. A. *J. Chem. Phys.* **1975**, *63*, 3228–3237.

(82) Singh, R. B.; Rai, D. K. *J. Phys. Chem.* **1965**, *69*, 3451–3462.

(83) Barrow, R. F.; Clark, T. C.; Coxon, J. A.; Yee, K. K. *J. Mol. Spectrosc.* **1974**, *51*, 428–449.

(84) Gerber, G.; Broida, H. P. *J. Chem. Phys.* **1976**, *64*, 3423–3437.

(85) Coxon, J. A. *J. Mol. Spectrosc.* **1974**, *50*, 142–165.

(86) Chase, M. W., Jr.; et al. *J. Phys. Chem. Ref. Data* **1985**, *14*, (Suppl. 1), JANAF Thermochemical Tables.

(69) Young, H. D. *Statistical Treatment of Experimental Data*; McGraw-Hill: New York, 1962; pp 115–120.

(70) Finlan, J. M.; Simons, G. *J. Mol. Spectrosc.* **1975**, *57*, 1–13.

Table VI. Reported r_{\min} and r_{\max} Values and Distances Calculated in This Work at the Reported Energies^a

H ₂ , ^b $\nu = 0-13$		Na ₂ , ^c $\nu = 0-50$		HF, ^d $\nu = 0-18$		KH, ^e $\nu = 0-21$		CsH, ^f $\nu = 0-24$		CsH, ^g $\nu = 0-15$	
RKR	calcd	RKR	calcd	RKR	calcd	RKR	calcd	rotless ^h	calcd	RKR	calcd
0.413	0.4124	2.1966	2.2004	0.6231	0.6231	1.5432	1.5425	1.754	1.7459	1.8005	1.8000
0.416	0.4155	2.2030	2.2072	0.6251	0.6252	1.5482	1.5476	1.756	1.7489	1.8134	1.8131
0.420	0.4198	2.2144	2.2192	0.6278	0.6279	1.5547	1.5539	1.759	1.7536	1.8275	1.8272
0.425	0.4252	2.2282	2.2335	0.6310	0.6311	1.5623	1.5613	1.763	1.7598	1.8428	1.8426
0.432	0.4318	2.2442	2.2501	0.6347	0.6348	1.5709	1.5699	1.774	1.7679	1.8595	1.8593
0.439	0.4398	2.2625	2.2688	0.6390	0.6392	1.5804	1.5794	1.774	1.7767	1.8777	1.8774
0.449	0.4492	2.2832	2.2899	0.6439	0.6441	1.5910	1.5899	1.777	1.7860	1.8975	1.8973
0.460	0.4604	2.3065	2.3136	0.6494	0.6496	1.6026	1.6014	1.786	1.7962	1.9194	1.9193
0.473	0.4737	2.3326	2.3399	0.6556	0.6558	1.6154	1.6140	1.796	1.8072	1.9437	1.9436
0.489	0.4898	2.3618	2.3692	0.6626	0.6628	1.6293	1.6279	1.807	1.8192	1.9710	1.9710
0.509	0.5097	2.3946	2.4020	0.6705	0.6707	1.6444	1.6430	1.820	1.8322	2.0020	2.0020
0.535	0.5355	2.4317	2.4390	0.6795	0.6797	1.6609	1.6595	1.834	1.8463	2.0378	2.0379
0.571	0.5716	2.4741	2.4811	0.6898	0.6900	1.6989	1.6979	1.850	1.8616	2.0804	2.0804
0.633	0.6338	2.5235	2.5299	0.7018	0.7020	1.7466	1.7457	1.886	1.8964	2.1329	2.1330
0.883	0.8821	2.5823	2.5880	0.7159	0.7161	1.8088	1.8079	1.930	1.9383	2.2027	2.2029
1.013	1.0121	2.6559	2.6603	0.7331	0.7333	1.8977	1.8970	1.984	1.9900	2.3154	2.3157
1.120	1.1188	2.7565	2.7592	0.7548	0.7550	2.0701	2.0695	2.054	2.0571	2.7067	2.7071
1.219	1.2183	2.9485	2.9486	0.7845	0.7846	2.4459	2.4452	2.152	2.1525	2.8887	2.8889
1.316	1.3154	3.2205	3.2204	0.8342	0.8342	2.7599	2.7587	2.337	2.3362	3.0294	3.0291
1.413	1.4128	3.4847	3.4865	1.0206	1.0199	2.9969	2.9947	2.730	2.7314	3.1543	3.1533
1.513	1.5128	3.6605	3.6635	1.1131	1.1115	3.2143	3.2118	3.055	3.0571	3.2708	3.2700
1.618	1.6173	3.8125	3.8162	1.1869	1.1847	3.4258	3.4243	3.298	3.2998	3.3823	3.3796
1.730	1.7288	3.9538	3.9577	1.2541	1.2515	3.6384	3.6391	3.517	3.5211	3.4907	3.4873
1.853	1.8509	4.0900	4.0936	1.3181	1.3154	3.7467	3.7489	3.729	3.7358	3.5973	3.5932
1.992	1.9895	4.2243	4.2275	1.3807	1.3780	3.8572	3.8614	3.940	3.9510	3.7028	3.6984
2.158	2.1549	4.3593	4.3616	1.4429	1.4404	3.9710	3.9773	4.156	4.1707	3.8079	3.8036
2.370	2.3685	4.4969	4.4983	1.5054	1.5033	4.0894	4.0977	4.267	4.2835	3.9131	3.9094
2.675	2.6828	4.6393	4.6397	1.5688	1.5674	4.2141	4.2243	4.382	4.3990	4.0190	4.0163
		4.7887	4.7880	1.6339	1.6332	4.3476	4.3595	4.501	4.5181	4.1261	4.1246
		4.9477	4.9461	1.7011	1.7015	4.4936	4.5065	4.626	4.6420	4.2348	4.2349
		5.1198	5.1173	1.7715	1.7729	4.6580	4.6708	4.756	4.7726	4.3457	4.3479
		5.3098	5.3061	1.8460	1.8485	4.8508	4.8605	4.895	4.9126	4.4598	4.4641
		5.5243	5.5187	1.9261	1.9295	5.0903	5.0907	5.048	5.0666		
		5.7735	5.7642	2.0139	2.0177	5.4138	5.3911	5.211	5.2425		
		6.0744	6.0566	2.1129	2.1162			5.386 ^h	5.4559		
		6.3178	6.2879	2.2286	2.2302			5.692	5.7119		
				2.3711	2.3654						
				2.5625	2.5482						

^a Distances in angstroms. To conserve space, not all levels are shown. For extent of dissociation, see Tables I and II. All reported potentials truncated at 98% of dissociation. ^b Reference 30. ^c Reference 35; every third level is shown (0-48), plus level 50. ^d Reference 42. ^e Reference 47; alternate levels are shown for 0-10, then all from 10-21. ^f Reference 66. Rotationless potential; alternate levels are shown for $\nu = 0-12$, then all up to 98% of dissociation. ^g Reference 49. ^h This point has been questioned and omitted in a subsequent recalculation;⁶⁷ we also omit it from Figure 3.

Å from the reported potential.⁷⁷ The performance of the calculation is poor with CuH (96%)⁸⁸ and with HgH (98%),⁸⁹ giving average deviations in energy of ± 4.37 and $\pm 2.27\%$ of D_e , respectively. Another example of poor agreement is Mg₂.⁹⁰

Evaluation

The results of Table I, with widely accepted potentials, show that the method proposed here is more accurate by an overall average factor of about 10 than the Lippincott function, the best previously available method.^{19,20} The consistency of the method is as important as its overall accuracy. The largest average deviation for any single species in Tables I and II is $\pm 1\%$ of D_e , while the Lippincott function shows individual average deviations in the range of $\pm 5-10\%$ for several species. The proposed method has proven to be reliable with all potentials tested.

Agreement between calculated and RKR energies is often better on the outer limb than on the inner one. For the entries of Tables I and II, the overall average deviations for the region $r < r_e$ are almost 3 times greater than those for $r > r_e$. This can be understood by considering that the same error in a given pair of RKR values of r_{\min} and r_{\max} creates a larger error in the energy calculated at r_{\min} for the sensitive, steeply rising inner limb than at r_{\max} for the more gently rising outer limb. The overall average

deviation for the outer limbs of all potentials in Table I is only $\pm 0.22\%$ of D_e , or ± 0.18 kcal/mol unnormalized. The maximum deviation from any single RKR energy value on the outer limbs for all the species of Table I is ± 1.21 kcal/mol for one of the levels of NO; more typical values of maximum deviations from a single RKR point are $+0.13$ kcal/mol in H₂,³⁰ -0.30 in N₂, $+0.53$ in CO, -0.12 in KH,⁴⁷ $+0.033$ in Na₂,³⁵ and $+0.075$ in Cs₂, where a positive sign indicates that the calculated value lies above the RKR energy. By comparison, also on the outer limbs, the Morse function shows a maximum deviation of -10.40 kcal/mol for one of the levels in N₂ and the Lippincott function $+14.62$ kcal/mol for one of the levels in CO.

Oxygen ($X^3\Sigma_g^-$) shows the largest average deviation in Table I. The inner limb is calculated particularly poorly, with an average deviation of $\pm 1.17\%$ of D_e . This results from the fact that eq 6 takes into account only the effective nuclear charge. The triplet nature of $^*O-O^*$ is disregarded in calculating the value of m , which in turn affects the exponent β for the inner limb. Thus, triplet repulsion at $r < r_e$ is underestimated, and the calculated curve rises less steeply than the actual potential. The same behavior appears with PH ($X^3\Sigma^-$), available to 48% of dissociation.⁹¹ We expect that this method cannot be as accurate with triplets as it is with other ground-state species, unless a term specific for triplet repulsion is added to eq 6. The doublets HO and NO are treated as well as singlet species in Table I, so is CN, when $D_e = 185.1$ kcal/mol and $r_e = 1.171$ Å are used (av dev = $\pm 0.59\%$ of D_e). The poorest performance of the method with a singlet seems to

(87) Griller, D.; Kanabus-Kaminska, J. M.; Maccoll, A. *J. Mol. Struct. THERMOCHEM* 1988, 163, 125-131.

(88) Castaño, F.; deJuan, J.; Martinez, E. *Spectrochim. Acta* 1982, 38A, 545-548.

(89) Stwalley, W. C. *J. Chem. Phys.* 1975, 63, 3062-3080.

(90) Li, K. C.; Stwalley, W. C. *J. Chem. Phys.* 1973, 59, 4423-4427.

(91) Whether $D_e = 69.77^78$ or 72.98^{25} kcal/mol is used.

be illustrated by HCl (Tables I and V); its isotopomers also give equivalent deviations.

Tables I and II demonstrate that the proposed method comfortably breaks the barrier of $\pm 1\%$ of D_e in overall agreement with known potentials, the worst case being $\pm 0.85\%$ with O_2 . In terms of absolute average deviations, the desired "chemical accuracy" of ± 1 kcal/mol has been attained, the worst case again being O_2 with ± 1.02 kcal/mol.

The accuracy of this method allows it to be compared favorably even to methods that require extensive knowledge of the specific potential being described. One of the most successful such methods is the extended Rydberg (ER) procedure that, in addition to the properties required by the Morse function, requires the values of the Dunham coefficients Y_{20} , Y_{11} , and Y_{01} .²⁵ Accurate values for the last three parameters can be obtained only from fitting several observed energy levels. The ER method was found to give good analytical descriptions of ground-state potentials in their valence region, superior to the Hulburt-Hirschfelder potential, which requires the same Dunham coefficients, or other functions studied. The method has been confirmed to be the most accurate among those procedures requiring the same number of parameters.²⁴ A tabulation of values for the ER input parameters has been given for all diatomics involving the elements up to Cl.²⁵ For all the species common to this tabulation and to Tables I and II, the calculated potentials of the method proposed here exhibit an overall superiority of over a factor of 2 over the ER results.⁹²

A purely curve fitting procedure, designated GMF5, with five freely adjustable parameters for each species, was found to fit known potentials with an overall accuracy 40% higher than that of the ER method and to be superior to any other curve-fitting routine utilizing five freely adjustable parameters.²⁴ Unlike the proposed method, curve-fitting procedures accommodate any systematic errors in reported potentials and can fit equally as well different potentials for the same species that are in disagreement with each other. Increasing the number to seven freely adjustable parameters for each potential gives average deviations from RKR results about half those of GMF5. Compared to the curve-fitting results published for 12 ground-state species with GMF5,²⁴ the potentials calculated here are superior for H_2 ,¹¹ Li_2 ,³¹ and HF ,⁴² approximately equivalent for $NaCs$, I_2 ,³⁷ and LiH ,⁶¹ and inferior for O_2 , Cs_2 , OH , CO , Na_2 ,⁵⁴ and Cl_2 .⁵⁹ Thus, the potentials calculated by the proposed method, without *any* adjustable parameters, match or surpass the accuracy of the best five-parameter curve-fitting procedure in half the cases.

Knowledge of the uncertainties in reported r_{\min} and r_{\max} values is required before the results given in Table V can be used to evaluate the accuracy of the method vs uncertainties in the given distance-energy points. Distance uncertainties are, evidently, difficult to calculate precisely, and few reported potentials include specific values. Examples of some published estimates follow: For Na_2 , uncertainties of up to ± 0.020 Å are estimated as the dissociation limit is approached;⁵⁸ at 96.5% of dissociation (outer limb), this amounts to ± 3 ppt. For LiH , increasing uncertainties of up to ± 0.020 Å are estimated at the largest reported turning point (5.0144 Å),⁶¹ equivalent to ± 4 ppt. Potential curves agreeing to within 0.001 Å have been considered to map each other exactly.⁵⁷

(92) The ER method obtains energies as a function of distance from $V(r) = -D_e(1 + a_1x + a_2x^2 + a_3x^3) \exp(-ax)$. The procedure for the calculation of the coefficients a_i is at least as involved as eqs 4-7 and is not always free of calculational ambiguities; in addition, the Dunham-type coefficients needed are not accurately known unless the energies are well established to high vibrational levels. The species compared are (average deviation of the ER procedure as percent of D_e in parentheses, compare with Tables I and II): H_2 , ref 30 (± 0.55); Li_2 , ref 32 (± 0.49); Li_2 , ref 56 (± 0.77); N_2 (± 0.22); O_2 (± 0.33); Na_2 , ref 35 (± 1.29); Cl_2 , ref 59 (± 1.54); LiH , ref 40 (± 1.08); LiH , ref 61 (± 1.10); HO (± 0.55); HF (± 0.47) ref 42; NaH , ref 45 (± 0.28); HCl , ref 46 (± 0.84); and CO (± 0.05). For Li_2 , O_2 , and Na_2 , the coefficients a_i tabulated in ref 25 were not calculated from the properties of the species and the Dunham coefficients but were optimized to fit the available RKR points. The ER approach is significantly superior in the case of O_2 , for which it utilized optimized coefficients. Using a_i values calculated from the properties of the species and the Dunham coefficients gives ± 0.68 and ± 1.38 for Li_2 , ± 0.99 for O_2 , and ± 1.92 for Na_2 .

For one of the CsH potentials,⁶⁶ specific uncertainty values have been given: ± 0.006 Å for all inner turning points and for the steeper section of the outer limb ($v = 0-17$) and about ± 0.030 Å for the shallow part of the outer limb ($v > 20$). This is equivalent to an average of ± 2.5 ppt for the first region and ± 5.1 in the second (beyond 92% of dissociation). Overall, for all reported distances, the average uncertainty implied is ± 2.8 ppt. Table V shows that our calculated potential agrees overall to within ± 3.4 ppt. Table VI shows the reported r_{\min} and r_{\max} values and those calculated by this method at the corresponding energies. For the inner limb, the average deviation between calculated and reported distances is ± 0.0069 Å, essentially the same as the reported uncertainty. For the points $v \geq 20$ of the outer limb (the last three entries in Table VI), the discrepancies are 0.032, 0.070, and 0.020 Å; the one point deviating significantly by more than the specified uncertainty of ± 0.030 Å has subsequently been questioned and discarded.⁶⁷ In this instance, one of the worst agreements in Table V, calculated and reported distances agree essentially to within the overall reported uncertainties.

Uncertainties in reported distance values may be estimated by a different and more pragmatic approach by comparing with each other potentials for the same species from different laboratories, from different time periods, and with different algorithms for obtaining r_{\min} and r_{\max} values. Comparison of two sets of RKR distances for N_2 , both covering $v = 0-19$ (51% of dissociation),^{33,93} gives an average deviation with each other of ± 1.21 ppt and a maximum deviation of 0.005 Å at any one point. Comparison of two sets for I_2 , covering 96% of D_e ,^{37,94} shows an average deviation of ± 3.4 ppt. Two sets for NO , covering $v = 0-22$ (66.9% of D_e), differ by an average of ± 5.76 ppt.⁵¹ Comparison of two sets for HF , covering $v = 0-18$ (98% of D_e),^{41,75} shows that distance values differ by an average of ± 2.0 ppt, with deviations in r_{\max} of 7, 11, and 16 ppt for the three highest vibrational energy levels (90-98% of D_e). Comparison of two sets of RKR distances for Li_2 , both covering 53% of D_e ,^{31,32a} shows an average deviation of reported distances of ± 0.92 ppt. Among more recent work, comparison of three sets of RKR results^{62,63,95} for NaH with the recommended⁴⁵ RKR potential showed excellent agreements of the order of ± 0.2 ppt for the domain in common (54% of D_e), except for $v = 0$ of one set.⁶³ On the other hand, two sets of recent results^{63,96} for KH compared to the recommended⁴⁵ RKR potential gave average deviations of ± 0.41 ppt for only 28% of D_e ⁹⁶ and ± 1.02 ppt for 72.6% of D_e .⁶³ While some reported potentials may be more reliable, the above considerations suggest that distance values of RKR potentials randomly selected from the literature can be expected to have uncertainties of about an average of ± 1 ppt, if they do not exceed 80% of dissociation. Uncertainties increase rapidly above this level, and an overall average of ± 1.5 ppt for a potential covering 95% of dissociation would be a conservative estimate.

The potentials in the first part of Table V cover an average of 80% of dissociation with an overall average deviation of ± 1.27 ppt between calculated and reported values of r_{\min} and r_{\max} . The second part of the table covers an average of 88% of dissociation with an overall average deviation of ± 1.65 ppt. This suggests that, overall, the accuracy of the proposed method is approaching the limits of uncertainty of many reported r_{\min} and r_{\max} values and is probably within a factor of about 2 of expected uncertainty limits.

Considerations of average deviations in Table V do not reveal an important aspect of the agreements obtained in some instances, when the calculated curve straddles the points given by different reported potentials for the same species. For the case of CsH, the four different potentials included in Table V demonstrate this fact in Figure 4, which shows the deviations in parts per thousand

(93) Vanderslice, J. T.; Mason, E. A.; Lippincott, E. R. *J. Chem. Phys.* **1959**, *30*, 120-136.

(94) Verma, R. D. *J. Chem. Phys.* **1960**, *32*, 738-749.

(95) Orth, B. F.; Stwalley, W. C.; Yang, S. C.; Hsieh, Y. K. *J. Mol. Spectrosc.* **1980**, *83*, 314-322.

(96) Yang, S. C.; Hsieh, Y. K.; Verma, K. K.; Stwalley, W. C. *J. Mol. Spectrosc.* **1980**, *83*, 304-310.

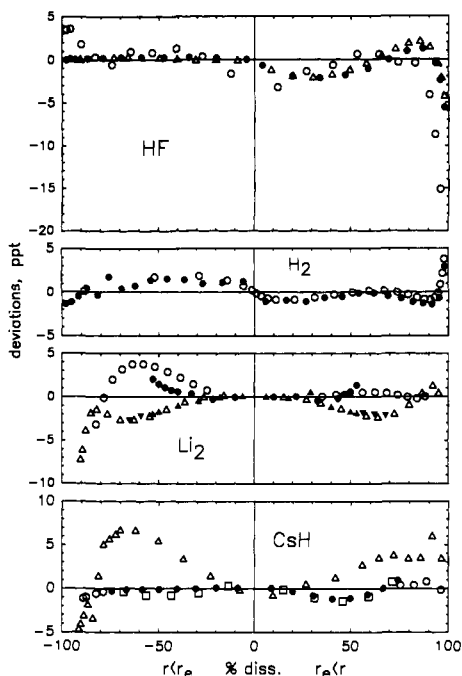


Figure 4. Deviations (ppt in distance) vs percent of dissociation. Deviations of the distances calculated in this work (horizontal zero line) from reported r_{\min} and r_{\max} values (representative points) at the same energies: left panels (negative values), inner limb; right panels, outer limb. HF: solid circles, RKR of ref 42; open circles, RKR of ref 75; triangles, RKR of DF from ref 43. H₂: solid circles, RKR of ref 30; open circles, ab initio of ref 11a. Li₂: solid circles, RKR of ref 31; solid triangles, IPA of ref 32a; inverse triangles, IPA of ref 32b; open circles, rotationless of ref 55; open triangles, rotationless of ref 56. CsH: solid circles, RKR of ref 49; open circles, hybrid of ref 67; triangles, rotationless of ref 66; squares, rotationless of ref 65.

of our calculated values from each CsH potential vs extent of dissociation. In straddling the reported values, the calculated curve (horizontal line) may be considered exact, within expected error, despite average deviations of ± 0.35 , ± 0.68 , ± 3.38 , and ± 0.51 ppt from each of the four CsH potentials (Table V). Thus, even though the agreement with one of the CsH potentials⁶⁶ represents one of the worst cases, the proposed method fits that potential close to the uncertainties reported for it and the calculated potential is apparently within the overall uncertainties of all four reported potentials. The case of CsH is not unique; similar straddling occurs in other cases, and Figure 4 shows a similar situation with Li₂. Nevertheless, this is not always the case, and Na₂ is an example where the calculated values deviate from the three potentials included in Table V generally in the same direction in the same regions. Figure 4 also shows the deviations between calculated and reported distances from various sources for HF and H₂. Plotting of energy deviations, as opposed to distance deviations, leads to patterns of straddling similar to those of Figure 4.

Equations 4–7 will now be considered. The proportionality constants of eqs 6 and 7 would be required in the formulation of any function in order to relate different units (kcal/mol, Å, mdy, Slater's effective nuclear charges, and Pauling's units of electronegativity) to the variation of β_- and β_+ and to weigh the relative importance of each property of the species. The form of eqs 4–7 is not unique, and the existing relationships may perhaps be described in a more elegant fashion. The number of constants involved should be judged in context with the number of individual RKR points against which this method has been tested successfully without adjustable parameters, well over 3000 points from over 50 potentials and many very different species including doublets and triplets. By contrast, an excellent fit for the 28 RKR points of H₂ has been reported with 16 freely adjustable parameters.⁹⁷

A shortcoming of the proposed method is the change in the functional form of β at r_c . Even though the function is continuous and the lowest vibrational level is far from r_c , the change does not allow the assignment of any significance to the higher derivatives of the function at that point.

The poor results obtained with CuH and HgH demonstrate another shortcoming that the method has in common with the Lippincott, Morse, and many other functions. Equation 1 cannot describe potential energy curves that exhibit one or more local maxima. Such curves have been described⁹⁸ as having a "hump" and can be viewed as having a significant energy of activation for bond formation between two atoms. For CuH, the reported⁸⁸ energy of the highest observed vibrational level is 4.7 kcal/mol greater than its reported⁹⁸ dissociation energy. Similarly for HgH, there is good evidence for a maximum.⁸⁹ The poor performance with Mg₂ demonstrates that the proposed method is not applicable to diatomic clusters or van der Waals molecules but is limited to description of valence bonding.

The calculation is not applicable to dissociations producing ionic products; it has been remarked that no known potential functions are applicable to such cases.^{7f} This shortcoming may be related to the fact that the third term of eq 7 defines a hyperbola. Values of $k_N r_N < 0.3 \times 10^{-3}$ mdy·mol²·kcal⁻² cannot be accommodated. It appears that the only molecules in that category are the alkali halides.

The use of Slater's effective nuclear charges in eq 6 introduces some uncertainty in that the charge calculated may be somewhat unreliable when high quantum numbers are reached,²⁸ but our method is not extremely sensitive to this.

The convenience of using Pauling's values of electronegativity,²⁷ given to one or two significant figures, also introduces some uncertainties, and the proposed method can be sensitive to this, depending on the species; we opted for the convenience.

Potentials of excited states have not been examined extensively. The proposed method appears overall superior to other available methods, but by a smaller margin. There are at least two reasons for this: (a) for species dissociating to excited-state atoms, Pauling's electronegativity values are not applicable, since the major component of electronegativity is the ionization potential; (b) for excited-state species, Slater's effective nuclear charge values will have to be calculated differently, depending on the state.

Finally, it should be noted that, unlike the Lippincott function, the proposed method does not treat H₂ as a unique case.

Extrapolations and ab Initio Results

The RKR and similar calculations cannot be used to extrapolate potentials beyond the region for which experimental information exists. Approaches for extrapolating known potentials include methods based on a perturbed Morse oscillator (PMO), methods based on essentially graphical extrapolations of reduced potential curves (RPC), and extrapolations based on exponential functions fitted to the known part of the inner limb of a potential, or polynomials in $1/r$ fitted to the known part of the outer limb. The long-range regions have been described by $V_{LR} = -\sum(C_n r^n)$, with $n = 6, 8, \text{ and } 10$, where the C_n are dispersion coefficients based on the proper multipole–multipole interactions; the gap between the known potential and the long-range region is filled with scaled ab initio results, the result being a "hybrid" potential.^{45,67} Below we compare some extrapolated, ab initio, and hybrid values to potentials predicted in this work.

The known part of the potential for CO has been extrapolated by Huffaker, utilizing the PMO approach,⁹⁹ and by Jenc and Brandt, utilizing the RPC approach for the inner limb only.¹⁰⁰ Ab initio values are also available.¹⁰¹ The available RKR results

(98) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold: New York, 1979; Vol. 4.

(99) Huffaker, J. N. *J. Mol. Spectrosc.* **1977**, *65*, 1–19.

(100) Jenc, F.; Brandt, B. A. *J. Mol. Spectrosc.* **1989**, *138*, 13–27.

(101) Cooper, D. L.; Kirby, K. *J. Chem. Phys.* **1987**, *87*, 424–432. This calculation obtains a value of $D_e = 253.20$ kcal/mol, or 2.33% lower than the currently accepted value. When the fractional falloff of energy with distance ($D_e = -1.000$) is considered in the region $r > r_c$, these results differ from our predicted values by an average of ± 0.007 , or $\pm 0.7\%$ of D_e .

(97) Beckel, C. L.; Kwong, R. B.; Hashemi-Attar, A. *J. Chem. Phys.* **1980**, *73*, 5385.

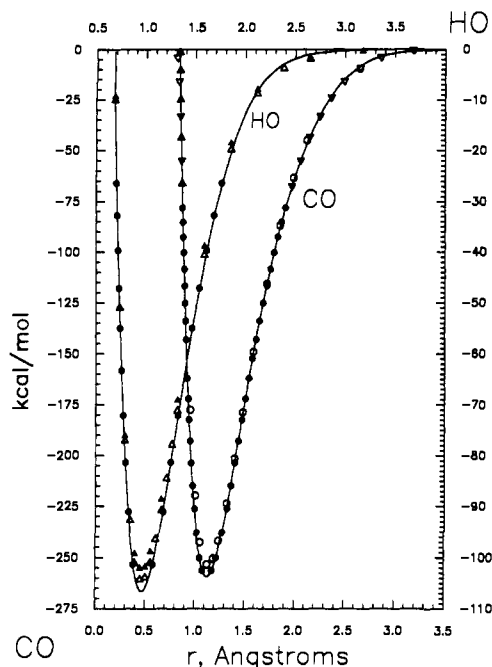


Figure 5. Energy (kcal/mol) vs distance (Å) for CO and HO: representative reported points. Left and bottom axes are for CO; right and top axes are for HO. CO: solid circles, RKR of ref 50; triangles, extrapolation of ref 100; inverse triangles, extrapolation of ref 99; open circles, ab initio of ref 101. HO: solid circles, RKR of ref 41; solid triangles, ab initio of ref 102b; open triangles, ab initio of ref 102a. The curves are the potentials calculated in this work.

to 69.9% of D_e , our predicted full potential, the ab initio results, and the two extrapolations of the RKR values are shown in Figure 5. The inner limb of the PMO extrapolation deviates significantly from the line predicted by our method, giving consistently shorter distances, by as much as 0.018 Å at 96.3% (average deviation ± 7 ppt, maximum deviation 21 ppt), while the extrapolation of the outer limb is in fair agreement. On the other hand, the RPC extrapolation, which has been successful in detecting errors or inaccuracies in experimentally determined potentials, is in good agreement with our predicted inner limb (average deviation ± 1.4 ppt, maximum deviation 1.6 ppt). Figure 5 also shows a similar comparison of our predicted potential for HO with the partial RKR potential⁴¹ and two ab initio calculations.¹⁰² The plots show that agreement between our predicted potentials and the ab initio results is reasonable for both CO and HO. While deviations between RKR points and our calculated potentials are not discernible in such plots, the deviations of the PMO extrapolation of the inner limb of CO are clearly seen, as are the deviations of the ab initio values from RKR results near the bottom of the potential well.

A hybrid potential for C₂H⁶⁷ has been included in Tables II and V and in Figure 4, showing good agreement; focusing on the regions above 75.5% of dissociation, agreement with our predicted distances is excellent: average deviations of ± 0.72 ppt for the extrapolation of the inner limb and ± 0.82 ppt for the hybrid portion of the outer.

Perhaps the most important aspect of extensions of RKR results involves the estimation of bond dissociation energies from partial potentials. Additional extrapolating techniques used in this context include the Birge-Sponer extrapolation¹⁰³ and the LeRoy-Bern-

Table VII. Bond Dissociation Energies (kcal/mol) Obtained from Partial RKR Potentials by Varying D_e to Minimize Average Deviation between Calculated and RKR Distances at Each Energy Level

species (ref)	D_e^a lit.	D_e^b calcd	dev, %	RKR, % dissocn	D_e , JANAF ^c
H ₂ (11)	109.49	109.22	-0.25	73.8 ^b	109.47
H ₂ (30)		108.70	-0.72	75.7 ^b	
Li ₂ (31)	24.36	24.45	+0.37	53.1	24.38 \pm 2.39
Li ₂ (32)		24.04	-1.31	67.9	
Li ₂ (55)		24.41	+0.21	74.1 ^b	
Li ₂ (56)		24.12	-0.99	75.1 ^b	
N ₂ (33)	228.43	229.84	+0.62	55.1	228.42
Na ₂ (35)	17.22	17.23	+0.05	75.0 ^b	17.06 \pm 0.29
Na ₂ (57)		17.24	+0.07	75.3 ^b	
Na ₂ (58)		17.22	-0.02	74.0 ^b	
Cl ₂ (59)	57.98	57.65	-0.56	74.3 ^b	57.98 (57.18) ^d
K ₂ (60)	12.70	12.77	+0.61	70.8 ^b	12.73 \pm 0.48
Rb ₂ (36)	11.29	11.49	+1.70	75.5 ^b	11.33 \pm 0.60
I ₂ (37)	35.88	35.44	-1.22	74.1 ^b	35.88
Cs ₂ (38)	10.43	10.39	-0.42	75.9 ^b	10.43 \pm 0.24
LiH (39)	58.01	58.48	+0.81	74.8	57.67 \pm 2.39
LiH (40)		58.45	+0.76	74.2 ^b	
LiH (61)		58.24	+0.40	72.2 ^b	
OH (41)	106.62	108.32	+1.62	75.2	106.72 \pm 0.29
HF (42)	141.19	141.22	+0.02	74.3 ^b	141.09 \pm 0.19
HF (75)		141.17	-0.01	74.3 ^b	
DF (43)	141.30	141.36	+0.04	73.1 ^b	
NaH (45)	45.46	45.65	+0.41	54.2	48.82 \pm 4.60
NaH (62)		45.73	+0.60	69.3	(45.46 \pm 0.29) ^e
NaH (63)		45.69	+0.50	73.9 ^b	(45.75) ^f
NaD (63)		45.59	+0.28	71.3 ^b	
NaH (95)		45.63	+0.36	54.2	
HCl (46)	106.49	103.56	-2.75	74.94 ^b	106.33
KH (47)	42.24	42.29	+0.11	72.6 ^b	44.52 \pm 3.50
KH (63)		42.31	+0.16	72.6	(42.32 \pm 0.14) ^f
KD (63)		42.33	+0.22	62.2	
RbH (45)	41.69	40.77	-2.19	57.4	NA (41.21) ^g
RbH (64)		40.99	-1.68	66.1	(41.69 \pm 1.72) ^e
RbH (48)		41.22	-1.13	74.4 ^b	(41.46) ^f
CsH (49)	42.29	42.21	-0.18	74.3	NA
CsH (65)		42.06	-0.56	71.3	(42.33) ^f
CsH (66)		43.04	+1.76	75.9 ^b	
CO (50)	259.25	255.83	-1.32	69.9	259.26
NO (51)	152.52	148.62	-2.55	66.9	152.77
NaK (68)	15.08	15.23	+0.99	70.3 ^b	NA
NaCs (52)	14.15	14.31	+1.09	74.0 ^b	NA (14.15 \pm 0.29) ^h
ICl (53)	50.13	49.65	-0.95	73.3 ^b	50.17

^a Values used for calculations of Tables I-VI. ^b Potential truncated at about 75% of complete dissociation. For rotationless potentials, the values given pertain to the outer limb. ^c Reference 86, JANAF Thermochemical Tables. D_e values were calculated from the values given for the thermodynamic bond strength (D_0 at 0 K) and the spectroscopic constants given: $D_e = D_0 + \omega_e/2 - (\omega_e x_e)/4$. NA indicates value not available in these tables. Uncertainties are given only when sizeable. Values in parentheses are from the sources indicated. ^d Jenc, ref 106. ^e Reference 45. ^f Reference 22, RPC approach; with the data of ref 63, this approach agrees with 42.89. ^g Pardo, A., et al. *Spectrochim. Acta* 1987, 43A, 887-893. ^h Value and error limits estimated in ref 53 by using different values of D_e to optimize the fit of the Hulburt-Hirschfelder function to the available potential of 94% of dissociation.

stein plots.¹⁰⁴ Varying D_e to obtain the best fit of a curve-fitting function to RKR results has also been used, for example, for NaCs with the Hulburt-Hirschfelder function.⁵² The method proposed here can also be used to estimate D_e from partial potentials. When all other properties required as input are known accurately, D_e can be varied to minimize deviations between RKR distances and distances calculated by this method at the RKR energies. This procedure was applied to the available RKR results for N₂ as a

(102) (a) Langhoff, S. R.; Werner, H.-J.; Rosmus, P. *J. Mol. Spectrosc.* 1986, 118, 507-529. This calculation obtains $D_e = 104.31$ kcal/mol, 2.14% lower than the currently accepted value. When the fraction of remaining energy ($D_e = -1.000$) at the ab initio distances is considered, these results differ from our predicted values by an average of ± 0.0057 , or $\pm 0.6\%$ of D_e . (b) Chu, S.-I.; Yoshimine, M.; Liu, B. *J. Chem. Phys.* 1974, 61, 5392. This calculation obtains $D_e = 102.22$ kcal/mol, 4.11% low. The fraction remaining energy at the ab initio distances differs from our predicted values by an average of ± 0.007 , or 0.7% of D_e .

(103) For a detailed discussion of the method and its applications and limitations, see: Gaydon, A. G. *Dissociation Energies and Spectra of Diatomic Molecules*; Chapman and Hall: London, 1968.

(104) LeRoy, R. J. In *Specialist Periodical Report: Molecular Spectroscopy*; Barrow, R. F., et al., Eds.; The Chemical Society: London, 1973; Vol. 1.

test case; the RKR potential is known only to 55.1% of dissociation. The value of D_e that minimizes the average deviation is 229.84 kcal/mol, only 0.62% higher than the currently accepted value of 228.43.⁸⁶ This result is remarkable for such a long extrapolation. The accuracy of this procedure was then tested with species whose D_e is fairly well known. Potentials reported to between 50 and 75% of D_e were used, along with potentials known to greater extents but truncated at a level near 75%. The value of D_e that minimizes the average deviation between calculated and reported r_{\min} and r_{\max} values was obtained and compared to the currently accepted values of D_e for 42 potentials in Table VII. The average deviation between the values of D_e so estimated and the currently accepted values for all entries in Table VII is under 1%, $\pm 0.8\%$ of D_e . The greatest deviation was obtained with the potential for HCl, -2.75% .¹⁰⁵ The average extent of dissociation for all entries in Table VII is only 71%. To our knowledge, this level of accuracy and consistency for predicting D_e from less than three quarters of the full potential is unprecedented. At the 70–75% level, it appears from Table VII that a reliable RKR potential can be used to estimate D_e with a better than 70% probability of accuracy to within $\pm 1\%$ of D_e and with confidence that the value would not be in error by more than $\pm 3\%$ at the *utmost*. With potentials known to 80–85% of dissociation, an analysis such as that presented in Table VII shows that the optimized D_e values obtainable deviate from currently recommended values by an overall average of only $\pm 0.6\%$ of D_e .

Accuracies of other types of extrapolations for obtaining D_e from RKR results may be compared in the following example: RKR potentials for NaH and NaD, known to 86.0 and 83.5% of D_e , respectively, led to extrapolated values of $D_e = 46.61 \pm 1.43$ and 47.75 ± 1.43 kcal/mol in significant disagreement with each other and with a sizeable uncertainty.⁶³ Using the same potentials with our procedure gives optimized values of $D_e = 45.46$ and 45.45 kcal/mol, in excellent agreement with each other and with the value of 45.46 ± 0.29 kcal/mol recommended recently on the basis of a review of all available evidence;⁴⁵ the JANAF Tables give 48.82 ± 4.6 kcal/mol.⁸⁶ Similarly, Birge-Sponer extrapolations of RKR results for KH and KD, extending to 73 and 62% of D_e , respectively, showed very poor agreement with each other and led to $D_e = 48.7 \pm 4.3$ kcal/mol.⁶³ Application of our procedure to the same results gives 42.31 and 42.33, respectively, in good agreement with each other, and with a critical review recommending 42.32 ± 0.14 kcal/mol,^{22b} with 42.25 ± 0.01 based on the full potential,⁴⁷ and 42.24 recommended recently.⁴⁵

The current substantial uncertainty in the value of $D_e(\text{RbH}) = 41.69 \pm 1.72$ kcal/mol⁴⁵ can be narrowed by this procedure, as an example. Optimizing D_e for fitting the available potential (78.3% of dissociation)⁴⁸ gives a value of 41.39 kcal/mol; this value along with the other results shown in Table VII for RbH point to 41.4 ± 0.5 as the best estimate. Similarly, for Rb_2 , the RPC approach^{22a} has led to $3870 \text{ cm}^{-1} < D_e < 4020 \text{ cm}^{-1}$ (11.29 ± 0.21 kcal/mol) on the basis of 83.9% of the potential.³⁶ Our optimization leads to $D_e = 11.41$ kcal/mol (3992 cm^{-1}), in excellent agreement with a recent experimental result of 11.42 kcal/mol (3993.5 cm^{-1}).¹⁰⁶ For NaCs, a fit of the RKR results to the Hulbert-Hirschfelder function gave $D_e = 14.153$ kcal/mol (4950 cm^{-1}),⁵² while a fit to our function leads to 14.185 kcal/mol (4961 cm^{-1}).

We do not recommend application of this procedure to estimating D_e from knowledge of less than 65% of the potential. In addition, on applying this procedure, the value of D_e must be varied significantly during minimization of the average deviation, in order to avoid being misled by local minima that can appear when there is scatter in the RKR points. Optimizing D_e to minimize energy deviations at reported RKR distances leads to similar, although marginally less accurate, results; it is not recommended, because energy deviations at high extents of dissociation are always very

(105) Oxygen is not included in Table VII. The two available potentials (68% of dissociation) lead to D_e values that are low by 3.09% (ref 34) and 2.88% (ref 71), confirming the poorer performance of the method with triplets.

(106) Amiot, C. Unpublished work cited by Jenc, F. *Phys. Rev. A* **1990**, *42*, 403–416.

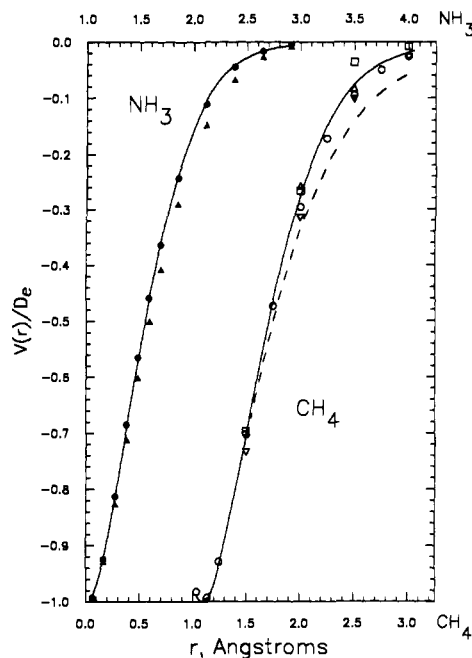


Figure 6. Energy normalized to $D_e = -1.000$ vs distance (Å) for $\text{CH}_3\text{-H}$ (open symbols) and $\text{NH}_2\text{-H}$ (filled symbols). CH_4 : circles, ab initio of ref 111; squares, ab initio of ref 109; triangles, ab initio of ref 110; inverse triangles, ab initio of ref 112. NH_3 : ab initio of ref 116; circles, 30° results; triangles, 0° results. The solid curves are our predicted potentials and the dashed curve the standard Morse potential for methane.

small and such points are disregarded, in effect.

Polyatomic Molecules

While RKR potentials, when available, are generally more reliable than ab initio calculations for diatomics, no RKR or similar potentials are obtainable for the breaking or making of one bond in polyatomic molecules. Analytic functions for such dissociations are useful for calculating energy barriers in reactions such as atom transfers by complex radicals,^{16,17} for generating potential energy surfaces,^{107,108} for trajectory calculations, etc. Various types of ab initio calculations have appeared for the dissociation of one bond in methane^{107–112} and in ammonia.¹¹³ The ability of analytic functions, derived for use with diatomics, to describe the dissociation curve in methane was examined by Brown and Truhlar,¹¹² and the conclusion was that functions such as those of Morse,¹⁸ Lippincott,¹⁹ Rydberg,² and Varshni⁶ do not deviate from the ab initio dissociation curve by more than they deviate from RKR results for diatomics, when each function was adjusted to fit exactly one ab initio point at 1.5 Å. The Lippincott and Varshni functions were found to give better overall fit, and all functions were found to overestimate bonding beyond 2.25 Å. Since ab initio calculations generally do not yield the correct D_e , comparisons were made on the basis of the fraction of bonding energy remaining at various C–H distances.

The procedure of comparing normalized energies is common with ab initio results, and we followed the same approach in comparing the predictions of our function with the several calculations available for dissociating $\text{CH}_3\text{-H}$ at different levels of theory. The results are shown in Figure 6. The ab initio cal-

(107) Hase, W. L.; Mondro, S. L.; Duchovic, R. J.; Hirst, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 2916–2922.

(108) Duchovic, R. J.; Hase, W. L.; Schlegel, H. B. *J. Phys. Chem.* **1984**, *88*, 1339–1347.

(109) Duchovic, R. J.; Hase, W. L.; Schlegel, H. B.; Frisch, M. J.; Raghavachari, K. *Chem. Phys. Lett.* **1982**, *89*, 120.

(110) Schlegel, H. B. *J. Chem. Phys.* **1986**, *84*, 4530–4534.

(111) Hirst, D. M. *Chem. Phys. Lett.* **1985**, *122*, 225–229.

(112) Brown, F. B.; Truhlar, D. G. *Chem. Phys. Lett.* **1985**, *113*, 441–446.

(113) McCarthy, M. I.; Rosmus, P.; Werner, H.-J.; Botschwina, P.; Vaida, V. *J. Chem. Phys.* **1987**, *86*, 6693–6700.

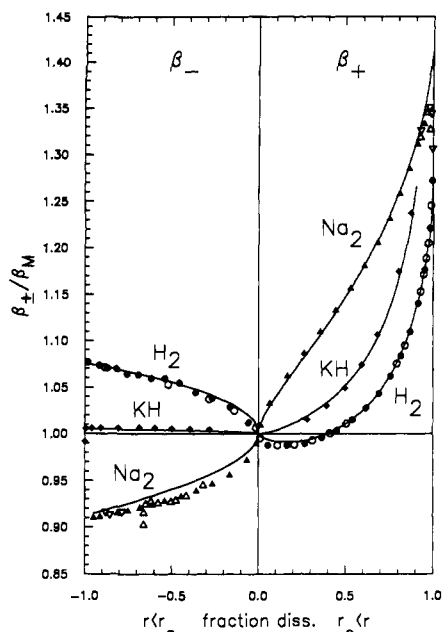


Figure 7. Ratio β_{\pm}/β_M vs fraction of dissociation. The points depict values of β_{\pm} calculated from the reported potentials by eqs 8 (left panels, inner limb) or 9 (right panels, outer limb). Representative points are shown. H_2 : solid circles, RKR of ref 30; open circles, ab initio of ref 11a. KH: solid rhombi, RKR of ref 47 (uncorrected). Na_2 : solid triangles, RKR of ref 35; open triangles, rotationless of ref 57; inverse triangles, rotationless of ref 58. The curves are calculated from eqs 4 (left panel) and 5 (right panel). Morse's β_M is the horizontal line at 1.00.

culations optimize the H-C-H angle of the methyl fragment as one C-H bond is stretched.¹¹⁴ In our calculation, account is taken of energy changes resulting from the hybridization change around C by calculating D_e as the thermodynamic dissociation energy for one C-H bond (D_0 at 0 K) plus half the sum of all fundamental frequencies of methane minus half the sum of all fundamentals for methyl, obtaining $D_e = 112.2$ kcal/mol, in agreement with a previous estimate of 112.4.¹¹⁵ While the various levels of theory of the ab initio calculations lead to somewhat different values, it has been concluded¹¹⁰ that the correct potential curve lies between the results of Duchovic et al.¹⁰⁹ and the Morse curve. With trivial cpu time, the proposed calculation predicts exactly this behavior.

A comparison with the ab initio calculations for H_2N-H ¹¹³ is also given in Figure 6, again in terms of normalized energies. Ab initio results have been reported at several different angles, θ , between the NH bond being stretched and the plane defined by the three atoms of the remaining H_2N fragment; Figure 6 shows the values reported for $\theta = 0$ and 30° and our predicted energies. With values for r_e , D_e , and ω_e obtained as for methane, our calculation predicts a potential near the 30° values, which is the most stable ab initio set of all decomposition angles reported.¹¹⁶ The average deviation in the normalized energy between our predicted values and those for 30° is only ± 0.004 , or $\pm 0.4\%$ of D_e . This high level of agreement is probably fortuitous, but does indicate, along with the results for methane, that bond breaking in polyatomic species is not qualitatively different from that in

(114) An interesting aspect of the ab initio calculations is that the fractional decrease in energy as a function of distance is not drastically different for optimized geometries compared to constant tetrahedral geometry throughout the H_3C-H bond stretching process. In our a priori calculation, the equivalent of not optimizing geometries would be to include only the stretching frequency of the C-H bond being broken in the calculation of D_e .

(115) The values of D_e obtained from the different ab initio calculations are 109.46 (ref 104 and 105), 110.6 (ref 106), 109.45 (ref 108), and 104.3 kcal/mol (ref 109).

(116) The energies reported for the 30° geometry are more stable at all distances compared to the 0° geometry (which implies a flat NH_3). The value of the experimental $D_e = 117.38$ kcal/mol was calculated as described for methane.

diatomics and that the method proposed here is capable of describing it.¹¹⁷

Discussion

While potential energy curves for different species appear similar, the subtle variations that exist led to pessimistic outlooks for success in formulating a universal potential energy function. The presentation of Figure 7 makes clear these variations in different species by showing the variability of β as a function of extent of dissociation. Equation 1 can be solved for β_{\pm} at each point of an RKR potential:

$$\beta_- = -\ln \{1 + [U(r)/D_e]^{1/2}\}/x \quad r < r_e \quad (8)$$

$$\beta_+ = -\ln \{1 - [U(r)/D_e]^{1/2}\}/x \quad r > r_e \quad (9)$$

where $U(r)$ and $x = r - r_e$ are the RKR values. The Morse function assumes constant β throughout the domain, $\beta = \beta_M$, as depicted by the horizontal line at unity in Figure 7. The points depict values of β_{\pm} obtained from the RKR potential by eq 8 or 9, normalized to β_M , for H_2 , KH, and Na_2 as typical examples (cf. Table VI). The curves in Figure 7 are given by eq 4 or 5, where u can be seen as a form of the Morse equation; at r_e , $\beta_{\pm} = \beta_M$. With high-quality potentials, the variation in the values of β_{\pm} obtained by eq 8 is always smooth and monotonic on the left limb; any scatter or change in direction indicates questionable RKR values, and Figure 7 shows a clear irregularity for the first point for KH,⁴⁷ which has been questioned on other grounds;⁶⁷ irregularities are seen in the rotationless results for Na_2 for distances less than 2.3692 Å,⁵⁷ and less than 2.2333 Å.⁵⁸ Figure 7 also shows some small scatter for the RKR points of H_2 on the inner limb, for which r_{min} values are reported to three significant figures. We have detected similar irregularities for several reported potentials, such as HO below 0.731 Å,⁴¹ Li_2 below 1.8656 Å,⁵⁶ and others.

The outer limb of Na_2 in Figure 7 shows a decrease in the values of β_+ at high extents of dissociation, beyond 96.6% of D_e (6.63 Å), as calculated from the rotationless potentials^{57,58} by eq 9. Similar declines in β_+ are obtained from the IPA potential for Cs_2 beyond 96.2% (9.35 Å), the RKR potential for I_2 beyond 89.7% (3.94 Å),³⁷ the rotationless potential for Cl_2 beyond 98.0% (3.61 Å),⁵⁹ the rotationless potential for Li_2 beyond 98.98% (7.18 Å),⁵⁶ and the rotationless potential for NaK beyond 97.4% (7.54 Å). Such decreases in β_+ are not apparent in the IPA potential for 7LiH extending to 99.4% (5.20 Å),⁶¹ the RKR potential of HF to 99.2% (2.87 Å),⁴² and the RKR potential of KH to 99.8% (6.98 Å).⁴⁷ The RKR potential of H_2 also produces no decline in β_+ up to the highest energy level, 99.6% of dissociation (3.26 Å); however, the values of β_+ calculated from the ab initio potential^{11a} for H_2 show a decline beyond 99.95% of dissociation (4.02 Å). These decreases in the values of β_+ obtained from reported potentials probably indicate the onset of "long range" behavior, beyond the valence region, rather than being artifacts in the reported potentials. Our calculation of β_+ , eq 5, does not take account of these declines at high extents of dissociation.

Values of m and n calculated from eqs 6 and 7 are given in Table VIII, along with additional data used in this work. The Morse function assumes constant β , equivalent to $m = 0$ and $n = \infty$; it describes adequately the inner limb of species such as KH (Figure 2), HCl, RbH, CsH, etc., which have m values near zero, and the available RKR potential of the outer limb of CO (Figure 2), which has the highest n value in Table VIII.

Among the properties of the species required as input for most of the existing potential energy functions D_e , ω_e , and r_e are theoretical constructs involving the bottom of the potential well. The latter two quantities are often derived from fitting some function to the lowest vibrational levels of the potential. There are alternative approaches when RKR potentials are not available: The internuclear distance is often known from crystallographic or

(117) Slater's effective nuclear charges for C and N were used to approximate the values for CH_3 and NH_2 . Group electronegativity values of CH_3 and NH_2 were used from Boyd, R. J.; Edgecombe, K. E. *J. Am. Chem. Soc.* 1988, 110, 4182-4186; 2.2 was used for H.

Table VIII. Data Used in This Work and Characteristic Coefficients from Equations 6 and 7^a

species	r_e , Å	ω_e , cm ⁻¹	(Z ₁)(Z ₂)	m	n
H ₂	0.741 44	4403.57	(0.70)(0.70)	0.084	2.39
⁷ Li ₂	2.673	351.43	(0.95)(0.95)	-0.067	0.73
⁶ Li ⁷ Li	2.673	365.76	(0.95)(0.95)	-0.067	0.73
N ₂	1.0977	2358.58	(3.45)(3.45)	-0.026	1.19
O ₂	1.207 54	1580.19	(4.20)(4.20)	-0.030	0.80
Na ₂	3.078	159.18	(1.85)(1.85)	-0.077	0.67
³⁵ Cl ₂	1.9879	559.75	(4.05)(4.05)	-0.050	0.70
K ₂	3.9244	92.41	(2.15)(2.15)	-0.098	0.63
⁸⁵ Rb ₂	4.2099	57.75	(2.15)(2.15)	-0.105	0.61
I ₂	2.6657	214.55	(6.65)(6.65)	-0.067	0.65
Cs ₂	4.646	42.02	(2.75)(2.75)	-0.116	0.60
⁶ LiH	1.595 56	1420.06	(0.95)(0.70)	0.039	1.79
⁷ LiH	1.595 56	1405.45	(0.95)(0.70)	0.039	1.79
HO	0.9696	3735.21	(0.70)(4.20)	0.032	1.88
HF	0.9168	4138.32	(0.70)(4.85)	0.060	3.20
DF	0.9168	2998.3	(0.70)(4.85)	0.060	3.21
NaH	1.8870	1171.76	(1.85)(0.70)	0.010	1.55
NaD	1.8870	847.7	(1.85)(0.70)	0.010	1.55
DCl	1.274 55	2145.2	(0.70)(4.05)	0.005	1.32
KH	2.2401	986.65	(2.15)(0.70)	0.005	1.59
KD	2.2401	708.1	(2.15)(0.70)	0.005	1.59
⁸⁵ RbH	2.3668	937.11	(2.15)(0.70)	0.002	1.57
CsH	2.4943	891.25	(2.75)(0.70)	0.004	1.68
CO	1.128 32	2169.52	(2.90)(4.20)	0.019	6.18
NO	1.150 76	1904.13	(3.45)(4.20)	-0.008	0.99
NaK	3.4968	124.01	(1.85)(2.15)	-0.083	0.65
NaCs	3.850	98.89	(1.85)(2.75)	-0.088	0.65
I ³⁵ Cl	2.321	382.18	(6.65)(4.05)	-0.037	0.77
H ₃ C-H	1.091	3117.6	(2.90)(0.70)	-0.005	1.30
H ₂ N-H	1.0124	3721.5	(3.45)(0.70)	0.017	1.49

^a Values for D_e are given in Tables V and VII. For methane and ammonia, the values of D_e used were 112.2 and 117.4 kcal/mol, respectively. Properties of the species were obtained from the latest available RKR potential or subsequent critical reviews (refs 22, 25, 45, and 86).

microwave measurements, as for polyatomic species. We find that the equilibrium frequency can be approximated with sufficient accuracy from the observed infrared stretching frequency, ν , by $\omega_e = \nu + \nu^2/2D_0$. The dissociation energy, D_e , is often estimated from thermodynamic measurements of D_0 (heats of formation through Hess's Law),⁸⁵ and we find an adequate approximation to be $D_e = D_0 + \nu/2 + 3\nu^2/16D_0$.¹¹⁸ These approximations lead to errors in D_e not greater than 0.01% of its value; the average error in ω_e is $\pm 0.2\%$, and the maximum is 0.6%. Generally, with polyatomic species, there is no alternative to using approximations such as these, and we used them to calculate ω_e for H₃C-H and H₂N-H from the observed infrared stretching frequencies.¹¹⁹ Using these approximations for D_e and ω_e with diatomics does not significantly affect the accuracy of the calculated potentials.¹²⁰

(118) The value of ω_e for methane has been calculated, and our value is in good agreement: Gray, D. L.; Robiette, A. G. *Mol. Phys.* 1979, 37, 1901-1920. Our value was calculated from the observed⁸⁶ fundamental stretching frequencies of $\nu_1 = 2916.5$ cm⁻¹ and $\nu_3 = 3018.7$ cm⁻¹ (triply degenerate), as follows: $\nu = \{1/4(\nu_1^2 + 3\nu_3^2)\}^{1/2} = 2993.48$ and $\omega_e = \nu + \nu^2/2D_0 = 3117.6$ cm⁻¹, with $D_0 = 36107.2$ cm⁻¹ (103.24 kcal/mol at 0 K, ref 86). For ammonia, $D_0 = 107.12$ kcal/mol, ref 86.

(119) By approximating $(\omega_e\chi_e) = \nu^2/4D_0$ and substituting into $\omega_e = \nu + 2(\omega_e\chi_e)$ and $D_e = D_0 + \omega_e/2 - (\omega_e\chi_e)/4$.

Transition-state modeling is often judged successful if it reproduces experimentally observed energies of activation or at least produces energies proportional to observed values. The question can be asked whether any significance can be attached to transition-state distances resulting from such a model,^{13,14} especially when activation energies also correlate well with, and can be described in terms of, properties of reactants and products.^{14,17} The answer must be in the negative, *unless* the model can be shown to produce correct distances for at least some known reaction coordinates. The method proposed here does so for the reaction coordinates of bond making or bond breaking. Transition-state modeling based on curves obtained by this method might be more reliable in terms of transition-state distances that will result. Methods that use potential curves to calculate activation energies include the BEBO calculation of Johnston and Parr¹⁶ and our work,¹⁷ both originally based to various extents on relatively unreliable Morse bonding and antibonding potentials.

Only three multiply bonded species satisfy the criteria for inclusion in Tables I and II. While N₂, CO, and NO do not show deviations greater than those obtained with singly bonded species, this is a small sample size, covering less than 70% of D_e in each case; the applicability of the method to all multiply bonded ground states to high extents of dissociation probably remains to be proven, as more potentials become available.

Conclusions

The feasibility of accurate calculations of potential energy curves in terms of properties of reactants and products appears to have been demonstrated. We have added effective nuclear charge and electronegativity to the properties of the species needed for an accurate description of chemical bonding. The effects of these two properties on spectroscopic quantities have been detected before.²⁰ In retrospect, it is not surprising that any successful calculation of potential energy curves would require consideration of nuclear charge, as well as ionization potential and electron affinity, which are reflected in the electronegativity.

There is some analogy between the proposed method and the RKR and similar calculations. The RKR procedure requires as input a set of constants and observed energy levels to produce corresponding distances, limited to the domain of observed energy. The proposed method requires a different set of constants and produces distances at any specified energies. At the same energies, reported RKR distances and these calculated by this method are in good agreement for ground-state diatomics.

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Supplementary Material Available: A listing of the programs used, written in BASIC, is available on request from A.A.Z. For a copy on diskette for IBM PS/2 and compatibles, please forward a blank. A version for the VAX-8600 can be provided through BITNET by addressing A.A.Z. at ZAVITSAS@LIUVAX.

(120) With these approximations, typical average deviations as percent of D_e are (cf. Table I) H₂, ± 0.18 ; ⁷Li₂ (ref 32), ± 0.31 ; N₂, ± 0.08 ; Cs₂, ± 0.70 ; ⁷LiH, ± 0.34 ; HF, ± 0.31 ; DF, ± 0.13 ; KH, ± 0.11 ; and CO, ± 0.12 .