

# Connection between the Ogilvie and the Murrell–Sorbie potential energy functions

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Formulas for relating the parameters of the Murrell–Sorbie and the Ogilvie potentials are developed herein. Unlike the Simons–Parr–Finlan function, the Ogilvie potential is more easily connected with the Murrell–Sorbie potential, as evident from the longer range of agreement. The relationship is useful for generating high order Ogilvie potentials that exhibit the dissociation energy without experimentation, and for using the Murrell–Sorbie parameters in molecular softwares that adopt the Ogilvie function in their algorithms. The relations are invertible so that Ogilvie parameters from spectroscopic data can be applied in molecular softwares that employ Murrell–Sorbie potentials.

**KEY WORDS:** Murrell–Sorbie, Ogilvie, parameter relationship, potential function

**MSC subject classification:** 41A58, 81V55, 92E99

## 1. Introduction

The Ogilvie potential energy function [1]

$$U_{\text{OGI}} = C\xi^2 \left( 1 + \sum_{i=1} c_i \xi^i \right); \quad \xi = \frac{r - R}{0.5(r + R)}, \quad (1)$$

can be viewed as a power series extension of the harmonic potential function

$$U_{\text{HAR}} = \frac{1}{2}k(r - R)^2, \quad (2)$$

whereby  $r$  and  $R$  are the bond length and the equilibrium bond length, respectively. The Ogilvie potential function can also be seen as an averaged form of the Dunham potential function [2]

$$U_{\text{DUN}} = A\xi^2 \left( 1 + \sum_{i=1} \alpha_i \xi^i \right); \quad \xi = \frac{r - R}{R} \quad (3)$$

and the Simons–Parr–Finlan (SPF) potential function [3]

$$U_{\text{SPF}} = B\xi^2 \left( 1 + \sum_{i=1} \beta_i \xi^i \right); \quad \xi = \frac{r-R}{r} \quad (4)$$

because

$$\xi_{\text{OGI}}^{-1} = \frac{\xi_{\text{DUN}}^{-1} + \xi_{\text{SPF}}^{-1}}{2}. \quad (5)$$

A relation between the Dunham and SPF potential functions was given by Thakkar [4] as

$$\xi = \text{sign}(p) \left[ 1 - \left( \frac{R}{r} \right)^p \right] \quad (6)$$

which simplifies to the Dunham and SPF functions by substituting  $p = -1$  and  $p = +1$ , respectively. Incorporation of the Ogilvie potential function was made possible by Molski et al. [5, 6] through

$$\xi = \frac{r-R}{ar + (1-a)R} \quad (7)$$

which reduces to the Dunham, SPF and Ogilvie potential functions when  $a = 0, 1$  and  $0.5$ , respectively. Using similar approach, four classical potential functions were generalized by Lim [7] as

$$\begin{aligned} \frac{U}{D} = & \frac{n^x S_2^{1-x}}{m^y S_1^{1-y} - n^x S_2^{1-x}} \left( \frac{R}{r} \right)^{my} \exp \left[ S_1 \left( 1 - \frac{r}{R} \right) (1-y) \right] \\ & - \frac{m^y S_1^{1-y}}{m^y S_1^{1-y} - n^x S_2^{1-x}} \left( \frac{R}{r} \right)^{nx} \exp \left[ S_2 \left( 1 - \frac{r}{R} \right) (1-x) \right] \end{aligned} \quad (8)$$

whereby the generalized potential functions of Lennard-Jones [8–10], Morse [11], Buckingham [12, 13] and Linnett [14, 15] are recovered upon substitution of  $(x, y) = (1, 1), (0, 0), (1, 0)$  and  $(0, 1)$ , respectively into equation (8). Although these relationships describe the analytical difference between the compared potential functions, they do not provide the link by which a set of parameters from one potential function can be converted into equivalent parameters of another potential function. A more comprehensive understanding on the difference between potential functions is to firstly relate their parameters, followed by observation of their plotted energy curve [16–19]. In the case of power series potential functions, relations between parameters of Dunham, SPF and Ogilvie potential functions have been reported in equations (4.267) and (4.273) of Ogilvie’s monograph [20]. In spite of the accurate potential energy

curves that power series give near to the minimum zone [21], they are not convergent as  $r \rightarrow \infty$ . Obviously the bond length range whereby the power series functions are reliable depends on the number of coefficients used. A long range description of the Ogilvie potential function has been given in equation (4.274) by Ogilvie [20] to enable a large number of coefficients to be extracted from Morse parameter, due to the latter's convergence as  $r \rightarrow \infty$ . Further improvement to these coefficients can be attained by expressing them in terms of Murrell–Sorbie parameters. The Murrell–Sorbie potential function, which converges as  $r \rightarrow \infty$ , has additional parameters that enable better fit to experimental data in comparison to the Morse potential function. This paper develops a set of equations that enable the extraction of Ogilvie coefficients from Murrell–Sorbie parameters.

## 2. Analysis

By adding two terms to the original Rydberg potential function [22, 23]

$$U_{\text{RYD}} = -D(1 + a\rho) \exp(-a\rho) \quad (9)$$

where  $\rho = r - R$  and  $D$  is the magnitude of the minimum well-depth, Murrell and Sorbie [24] proposed an extended version of the Rydberg function as

$$U_{\text{MS}} = -D \left( 1 + \sum_{i=1}^n a_i \rho^i \right) \exp(-a_1 \rho) \quad (10)$$

where  $n = 3$ . We note that

$$(U_{\text{MS}})_{r=R} = -D \quad (11)$$

while

$$(U_{\text{OGI}})_{r=R} = 0. \quad (12)$$

Hence the Murrell–Sorbie potential function is uniformly increased by  $D$  to become the Shifted Murrell–Sorbie (SMS) potential function

$$U_{\text{SMS}} = D - D \left( \sum_{i=0}^{\infty} a_i \rho^i \right) \exp(-a_1 \rho), \quad (13)$$

where  $a_0 = 1$ , for enabling comparison with Ogilvie potential function. We let  $n \rightarrow \infty$  to offer a more generalized analysis although, for practical reason, we impose  $a_{n>3} = 0$  at a later stage. Equation (13) can be recasted into a different form

$$U_{\text{SMS}} = D \left[ \exp(+a_1 \rho) - \sum_{i=0}^{\infty} a_i \rho^i \right] \exp(-a_1 \rho) \quad (14)$$

whereby substitution of

$$\exp(\pm a_1 \rho) = \sum_{i=0}^{\infty} (\pm 1)^i \frac{(a_1 \rho)^i}{i!} \tag{15}$$

into equation (14) gives

$$\frac{U_{\text{SMS}}}{D} = \left[ \sum_{i=2}^{\infty} \left( \frac{a_1^i}{i!} - a_i \right) \rho^i \right] \sum_{i=0}^{\infty} \frac{(-a_1 \rho)^i}{i!}. \tag{16}$$

Rearrangement of equation (16) in increasing order of  $\rho$  and imposing  $a_{n>3} = 0$  leads to

$$\frac{U_{\text{SMS}}}{D} = \sum_{i=0}^{\infty} \left( \frac{(-a_1)^{i+2}}{i! + (i+1)!} + \sum_{j=0}^i (-1)^{i+j-1} \frac{a_1^{i-j} a_{j+2}}{(i-j)!} \right) \rho^{i+2}. \tag{17}$$

In the present analysis, we express the Ogilvie potential function in a slightly more concise form

$$U_{\text{OGI}} = C \sum_{i=0}^{\infty} c_i \xi^{i+2} \tag{18}$$

whereby  $c_0 = 1$ . Substituting the positive integer powers of  $\xi$  as either

$$\xi^i = \sum_{j=0}^{\infty} \left(-\frac{1}{2}\right)^j \binom{i+j-1}{i-1} \left(\frac{\rho}{R}\right)^{i+j} \tag{19}$$

or

$$\xi^i = \sum_{j=0}^{\infty} \left(-\frac{1}{2}\right)^j \binom{i+j-1}{j} \left(\frac{\rho}{R}\right)^{i+j} \tag{20}$$

into equation (18) allows the Ogilvie potential function to be expanded as power series of  $(\rho/R)$  instead of  $\xi$ . Regrouping terms with equal power of  $(\rho/R)$  leads to

$$\frac{U_{\text{OGI}}}{C} = \sum_{i=0}^{\infty} \sum_{j=0}^i \left(-\frac{1}{2}\right)^{i-j} \binom{i+1}{j+1} c_j \left(\frac{\rho}{R}\right)^{i+2}. \tag{21}$$

Since  $C \neq D$ , comparison of terms cannot be performed between equations (17) and (21). To compare terms, the first term on the RHS of both equations

must be brought to a common term, i.e.,  $\rho^2$ . Hence equations (17) and (21) are expressed as

$$\left(\frac{a_1^2}{2} - a_2\right)^{-1} \frac{U_{SMS}}{D} = \left(\frac{a_1^2}{2} - a_2\right)^{-1} \sum_{i=0}^{\infty} \left( \frac{(-a_1)^{i+2}}{i! + (i+1)!} + \sum_{j=0}^i (-1)^{i+j-1} \frac{a_1^{i-j} a_{j+2}}{(i-j)!} \right) \rho^{i+2} \tag{22}$$

and

$$\frac{R^2}{C} U_{OGI} = \sum_{i=0}^{\infty} \sum_{j=0}^i \left(-\frac{1}{2}\right)^{i-j} \binom{i+1}{j+1} c_j \frac{\rho^{i+2}}{R^i}, \tag{23}$$

respectively. Comparison of terms between equations (22) and (23) leads to

$$C = DR^2 \left(\frac{a_1^2}{2} - a_2\right) \tag{24}$$

and

$$c_i = f(R, a_1, a_2, a_3, i) + g(i) \tag{25}$$

whereby

$$f(R, a_1, a_2, a_3, i) = (-R)^i \left(\frac{a_1^2}{2} - a_2\right)^{-1} \left( \frac{a_1^{i+2}}{i! + (i+1)!} - \frac{a_1^i a_2}{i!} + \frac{a_1^{i-1} a_3}{(i-1)!} \right) \tag{26}$$

and

$$g(i) = \sum_{j=0}^{i-1} \frac{(-1)^{1+i-j}}{2^{i-j}} \binom{i+1}{j+1} c_j. \tag{27}$$

For convenience the first eight coefficients, except  $c_0 = 1$ , are furnished as follows:

$$c_1 = -R^1 \left(\frac{a_1^2}{2} - a_2\right)^{-1} \left( \frac{a_1^3}{3} - \frac{a_1 a_2}{1} + \frac{a_3}{1} \right) + \frac{2}{2^1} c_0 \tag{28a}$$

$$c_2 = +R^2 \left(\frac{a_1^2}{2} - a_2\right)^{-1} \left( \frac{a_1^4}{8} - \frac{a_1^2 a_2}{2} + \frac{a_1 a_3}{1} \right) - \frac{3}{2^2} c_0 + \frac{3}{2^1} c_1 \tag{28b}$$

$$c_3 = -R^3 \left( \frac{a_1^2}{2} - a_2 \right)^{-1} \left( \frac{a_1^5}{30} - \frac{a_1^3 a_2}{6} + \frac{a_1^2 a_3}{2} \right) + \frac{4}{2^3} c_0 - \frac{6}{2^2} c_1 + \frac{4}{2^1} c_2 \tag{28c}$$

$$c_4 = +R^4 \left( \frac{a_1^2}{2} - a_2 \right)^{-1} \left( \frac{a_1^6}{144} - \frac{a_1^4 a_2}{24} + \frac{a_1^3 a_3}{6} \right) - \frac{5}{2^4} c_0 + \frac{10}{2^3} c_1 - \frac{10}{2^2} c_2 + \frac{5}{2^1} c_3 \tag{28d}$$

$$c_5 = -R^5 \left( \frac{a_1^2}{2} - a_2 \right)^{-1} \left( \frac{a_1^7}{840} - \frac{a_1^5 a_2}{120} + \frac{a_1^4 a_3}{24} \right) + \frac{6}{2^5} c_0 - \frac{15}{2^4} c_1 + \frac{20}{2^3} c_2 - \frac{15}{2^2} c_3 + \frac{6}{2^1} c_4 \tag{28e}$$

$$c_6 = +R^6 \left( \frac{a_1^2}{2} - a_2 \right)^{-1} \left( \frac{a_1^8}{5760} - \frac{a_1^6 a_2}{720} + \frac{a_1^5 a_3}{120} \right) - \frac{7}{2^6} c_0 + \frac{21}{2^5} c_1 - \frac{35}{2^4} c_2 + \frac{35}{2^3} c_3 - \frac{21}{2^2} c_4 + \frac{7}{2^1} c_5 \tag{28f}$$

$$c_7 = -R^7 \left( \frac{a_1^2}{2} - a_2 \right)^{-1} \left( \frac{a_1^9}{45360} - \frac{a_1^7 a_2}{5040} + \frac{a_1^6 a_3}{720} \right) + \frac{8}{2^7} c_0 - \frac{28}{2^6} c_1 + \frac{56}{2^5} c_2 - \frac{70}{2^4} c_3 + \frac{56}{2^3} c_4 - \frac{28}{2^2} c_5 + \frac{8}{2^1} c_6 \tag{28g}$$

$$c_8 = +R^8 \left( \frac{a_1^2}{2} - a_2 \right)^{-1} \left( \frac{a_1^{10}}{403200} - \frac{a_1^8 a_2}{40320} + \frac{a_1^7 a_3}{5040} \right) - \frac{9}{2^8} c_0 + \frac{36}{2^7} c_1 - \frac{84}{2^6} c_2 + \frac{126}{2^5} c_3 - \frac{126}{2^4} c_4 + \frac{84}{2^3} c_5 - \frac{36}{2^2} c_6 + \frac{9}{2^1} c_7 \tag{28h}$$

A schematic representation of equation (28) is furnished in figure 1(a) whereby the numerators of the summative terms are reflected in the inner Pascal Triangle, i.e., all elements of the Pascal Triangle except  $\binom{n}{0}$  and  $\binom{n}{n}$ , while the

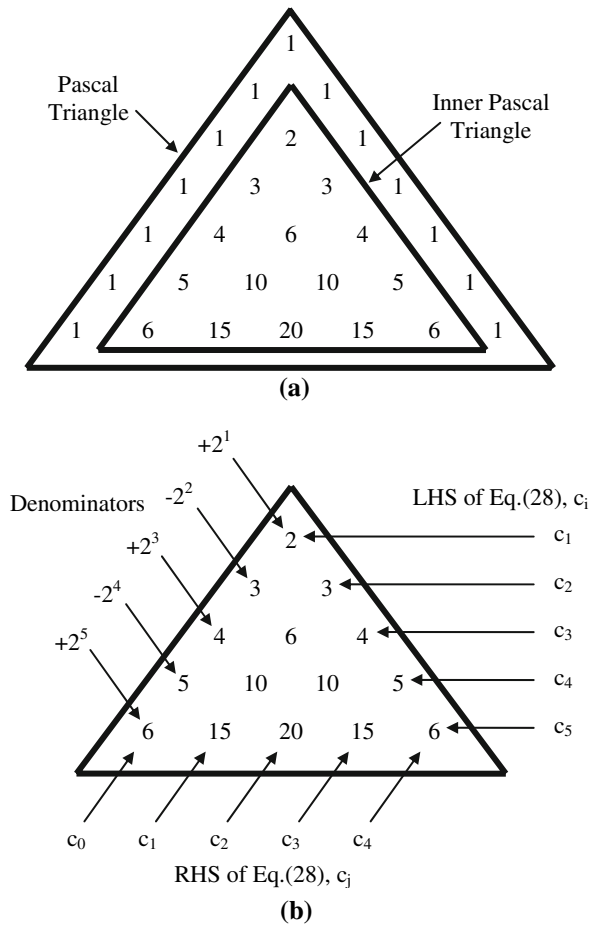


Figure 1. (a) An inner Pascal Triangle that excludes  $\binom{n}{0}$  and  $\binom{n}{n}$ , and (b) its application in representing the numerators for the summative part of equation (28).

denominators are powers of 2, as indicated in figure 1(b). The LHS of equation (28) corresponds to the summation of all elements in row  $(i + 1)$  for obtaining  $c_i$ , except  $\binom{n}{0}$  and  $\binom{n}{n}$ , while the diagonal columns  $(j + 1)$  correspond to the multiplier  $c_j$  on the RHS of equation (28).

### 3. Results and discussion

Verification of equations (24)–(28) is achieved by comparing the potential energy curves of Murrell–Sorbie and the Ogilvie potential energy functions using on the former’s parameters. Based on Huxley and Murrell’s [25] parameters, the SMS potential energy curves were plotted for the AIX diatomic molecules where

Table 1  
Murrell–Sorbie parameters by Huxley and Murrell [25] and the converted Ogilvie coefficients for AlX.

	AlAl	AlCl	AlF	AlH	AlO	AlS
$D(eV)$	1.572	5.15	6.94	3.163	5.33	3.878
$R(\text{Å})$	2.466	2.1301	1.6544	1.6478	1.6179	2.029
$a_1(\text{Å}^{-1})$	2.634	2.15	2.479	2.316	2.409	2.634
$a_2(\text{Å}^{-2})$	1.536	1.052	1.172	1.084	-0.418	0.827
$a_3(\text{Å}^{-3})$	0.038	0.824	1.484	0.576	1.106	0.466
$C(eV)$	18.47845	29.42518	36.10429	13.72352	46.31499	42.17947
$c_1$	-1.65829	-2.17167	-2.1829	-1.27521	-2.30097	-2.36317
$c_2$	-0.75635	3.238903	2.885371	0.775016	2.1753	2.523343
$c_3$	3.958839	-2.7609	-1.6635	-0.29745	-0.48466	-1.41787
$c_4$	-2.95143	0.18888	-0.4787	-0.13636	-0.50753	0.222698
$c_5$	-0.28465	0.914099	0.518513	0.118608	0.079574	0.273991
$c_6$	0.858706	0.084266	0.282231	0.084579	0.161698	-0.09734
$c_7$	0.166837	-0.25669	-0.04764	-0.00257	0.041194	-0.09041
$c_8$	-0.19313	-0.13301	-0.1067	-0.02877	-0.02493	0.008433

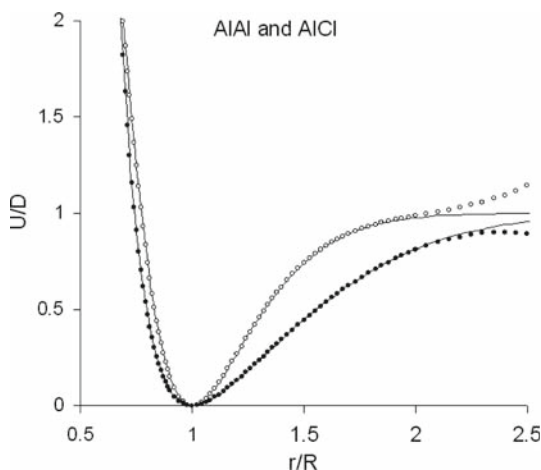


Figure 2. Comparison between the Murrell–Sorbie (curves) and Ogilvie (circles) based on the former's parameters for AlAl (open circles) and AlCl (closed circles).

X is Al, Cl, F, H, O and S. The Ogilvie coefficients were generated up to  $c_8$ . A list of Murrell–Sorbie parameters by Huxley and Murrell [25] and the converted Ogilvie coefficients for AlX is furnished in table 1.

Figures 2 to 4 show the potential energy curves for the six diatomic molecules whereby the continuous lines and discrete circles refer to the SMS and Ogilvie potential functions, respectively. The good agreement observed between both potential energy curves validates the developed relationship between



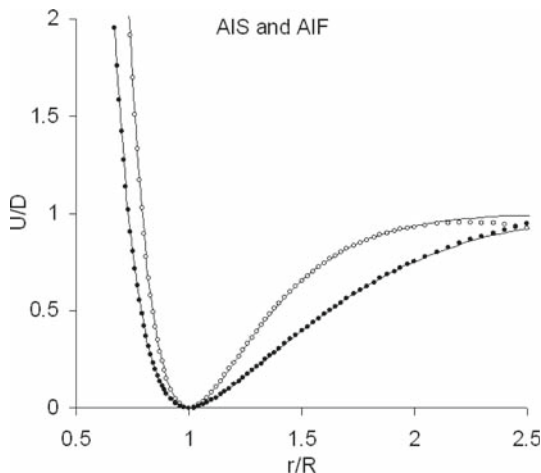


Figure 3. Comparison between the Murrell–Sorbie (curves) and Ogilvie (circles) based on the former’s parameters for AIS (open circles) and AIF (closed circles).

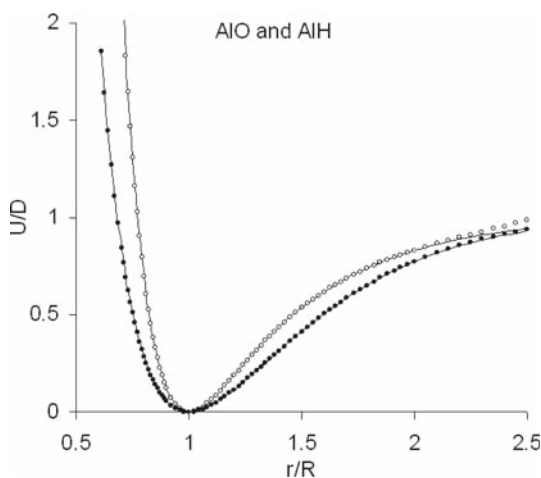


Figure 4. Comparison between the Murrell–Sorbie (curves) and Ogilvie (circles) based on the former’s parameters for AIO (open circles) and AIH (closed circles).

parameters of the two potential energy functions. Based on the plotted examples, the range of good agreement is found for  $r \leq 2R$  for AIAI and AIS,  $r \leq 2.25R$  for AIO and AICI, and  $r \leq 2.5R$  for AIF and AIH, when the Ogilvie coefficients are considered up to  $c_8$ . This range is significantly more superior to that between the SPF and Murrell–Sorbie potential functions, which are accurate within  $r = R \pm 0.1R$  [26].

#### 4. Conclusions

Extracting parameters of a potential function from parameters of another potential function is a cost effective and time saving method to plot the former's potential energy curve with reasonable accuracy compared to exhaustive experimentation. In this paper, coefficients of the Ogilvie potential functions  $c_i$  are expressed in terms of ( $i$ ) parameters of the Murrell–Sorbie potential function, and its lower order coefficients  $c_j$  ( $0 < j < i$ ). Comparison of the Ogilvie and the SMS potential energy curves for AlAl, AlCl, AlF, AlH, AlO and AlS show very good agreement when the Ogilvie parameters used are up to the  $c_8$  term. The relationships developed also suggest that the Murrell–Sorbie parameters can also be extracted from the Ogilvie coefficients. However, the absence of convergence as  $r \rightarrow \infty$  for the Ogilvie potential function would not provide the equal level of confidence as the conversion of Murrell–Sorbie parameters into Ogilvie coefficients furnished herein.

#### References

- [1] J.F. Ogilvie, Proc. Royal Soc. Lond. A 378 (1981) 287.
- [2] J.L. Dunham, Phys. Rev. 41 (1932) 721.
- [3] G. Simons, R.G. Parr and J.M. Finlan, J. Chem. Phys. 59 (1973) 3229.
- [4] A.J. Thakkar, J. Chem. Phys. 62 (1975) 1693.
- [5] M. Molski, J. Mol. Spectrosc. 193 (1999) 244.
- [6] M. Molski and J. Konarski, Int. J. Quant. Chem. 90 (2002) 183.
- [7] T.C. Lim, Chem. Phys. 320 (2005) 54.
- [8] J.E. Lennard-Jones, Proc. Roy. Soc. Lond. A 106 (1924) 463.
- [9] R. Mecke, Zeit. Physik 42 (1927) 390.
- [10] G.B.B.M. Sutherland, Proc. Indian Acad. Sci. 8 (1938) 341.
- [11] P.M. Morse, Phys. Rev. 34 (1929) 57.
- [12] R.A. Buckingham, Proc. Roy. Soc. Lond. A 168 (1938) 264.
- [13] C.K. Wu and C.T. Yang, J. Phys. Chem. 48 (1944) 295.
- [14] J.W. Linnett, Trans. Faraday Soc. 36 (1940) 1123.
- [15] J.W. Linnett, Trans. Faraday Soc. 38 (1942) 1.
- [16] T.C. Lim, Zeit. Naturforsch. A 58 (2003) 615.
- [17] T.C. Lim, Phys. Scripta 70 (2004) 347.
- [18] T.C. Lim, J. Math. Chem. 38 (2005) 195.
- [19] T.C. Lim, Mol. Phys. 104 (2006) 1827.
- [20] J.F. Ogilvie, *The Vibrational and Rotational Spectrometry of Diatomic Molecules* (Academic Press, San Diego, 1998) pp. 203–205.
- [21] J.J. Camacho, A. Pardo and J.M.L. Poyato, J. Chem. Soc. Faraday Trans. 90 (1994) 23.
- [22] R. Rydberg, Zeit. Physik 73 (1931) 376.
- [23] R. Rydberg, Zeit. Physik 80 (1933) 514.
- [24] J.N. Murrell and K.S. Sorbie, J. Chem. Soc. Faraday Trans. II 70 (1974) 1552.
- [25] P. Huxley and J.N. Murrell, J. Chem. Soc. Faraday Trans. II 79 (1983) 323.
- [26] T.C. Lim, Chem. Phys. 331 (2007) 270.