Radial functions of the diatomic metal hydrides AgH, GaH, InH and TlH from vibration-rotational spectra

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Received 17 December 1991

The coefficients c_j , $0 \le j \le 6$ or 8, defining the potential energy V(z) and coefficients of other radial functions related to adiabatic and nonadiabatic effects have been determined for the diatomic metal hydrides AgH, GaH, InH and TlH in their electronic ground states X ¹ Σ by a direct fit to the published wavenumbers of vibration-rotational transitions. The functions which are valid in specified ranges of internuclear distance depending on the molecule serve to reproduce the reported wavenumbers of the transitions within the uncertainty of the measurements. Comparisons are made with the fits of parameters reported by Urban, Birk, Polomsky and Jones.

1. Introduction

To determine directly from the measured wavenumbers of the pure rotational and vibration-rotational transitions the functions of the internuclear distance that represent not only the potential energy but also the adiabatic and nonadiabatic effects of diatomic molecules, we have developed a procedure that is based on analytic relationships between the coefficients of these functions in the convenient form of truncated polynomials and the energies of the vibration-rotational states within a particular electronic state. We have applied this procedure to a few molecular species not only as instances of how the applicable functions serve to represent the spectral data in both the most compact and the most physically meaningful form [1], but also to demonstrate that these functions are useful to predict unmeasured transitions within, and even somewhat beyond, the range of energy of the measured transitions, but particularly for isotopic variants for which experimental data are lacking.

In the case of the relatively light hydride species LiH, frequencies or wavenumbers of both pure rotational and vibration-rotational transitions, 584 in total for four isotopic variants, were known, from which five different radial functions were significantly determined [2]. For the nonhydride species

SiS, again both pure rotational and vibration-rotational transitions, 3025 in total for five isotopic variants, had been reported, but in this case no functions to describe the rotational nonadiabatic effects could be determined [3]; moreover the coefficients of the other two functions to take into account the partial breakdown of the Born-Oppenheimer approximation were determined by primarily the 33 pure rotational transitions. For the other nonhydride species LiCl and LiBr, in each case both pure rotational and vibration-rotational transitions had been measured in the microwave and mid-infrared spectral regions respectively. For LiCl four coefficients belonging to the radial function describing the variation of collectively the adiabatic and vibrational nonadiabatic effects associated with the motion of the Li nucleus were determined, but only one coefficient of each of two other functions, one for the corresponding effects associated with the Cl nucleus and another for the rotational nonadiabatic effects of the Li nucleus [4]; for all these six coefficients the 68 pure rotational transitions of the four isotopic variants weighed heavily in their significant determination, whereas the 2602 vibration-rotational transitions determined essentially the nine coefficients of the potential energy function. For LiBr, although 14 microwave lines and 1004 infrared lines up to v=9 and J=90 of four isotopic variants were

available for analysis, only seven coefficients of the potential energy function could be determined [4]. In each case of the four metal-hydride compounds AgH [5], GaH [6], InH [7] and TlH [8] and the corresponding deuterides [9], vibration-rotational transitions of four isotopic variants have been reported, but in no case have pure rotational lines been measured. Therefore the question arises whether only the vibration-rotational transitions suffice for the determination of the radial functions for the adiabatic and nonadiabatic effects. Because the latter are relatively much smaller than the dominant effects in the vibration-rotational spectra attributed to the potential energy function, the significant determination of the functions depends on both the relatively high resolution of the spectra and the great precision of the wavenumber measurements. As the spectra of these four metal hydrides were measured with tunable diode lasers [5-9], these conditions of high resolution and precision prevailed; despite the relatively few lines (one or two hundred, compared with the several hundreds or thousands in the previous cases [2-4]), we have succeeded to define accurately several coefficients of the applicable functions for each molecular species. We present here these results.

2. Summary of the method

We recall here the salient features of the procedure as a basis to understand these results of the metal hydride molecules. The effective potential energy governing the internuclear vibration and rotation (about the centre of molecular mass) of a diatomic molecule within a particular electronic state of type ${}^{1}\Sigma$ contains five radial functions and is expressed [10]

$$V_{\text{eff}} = c_0 z^2 \left(1 + \sum_{j=1}^{j} c_j z^j \right) + \sum_{j=1}^{j} m_e h_j^a z^j / M_a$$

+ $\sum_{j=1}^{j} m_e h_j^b z^j / M_b + B_e J (J+1)$
× $\left(1 + \sum_{j=0}^{j} m_e g_j^a z^j / M_a + \sum_{j=0}^{j} m_e g_j^b z^j / M_b \right) R_e^2 / R^2,$
(1)

in which m_e is the electronic rest mass, M_a and M_b are the masses of the separate atoms of types a and b distinguished by their atomic numbers, and the reduced variable z for displacement of internuclear separation R from the equilibrium distance R_e is defined [11,12]

$$z \equiv 2(R - R_{\rm e})/(R + R_{\rm e})$$
 (2)

The functions involving the coefficients $h_i^{a,b}$ take empirically into account collectively mostly the adiabatic effects, that the potential energy depends on not only the relative separation of the nuclei but also their momenta, and the nonadiabatic effects related to the vibrational inertia of the electrons, because other effects have different dependences on atomic mass which makes them currently negligible with respect to the experimental error of frequency measurements [10]. The functions involving the coefficients $g_i^{a,b}$ take empirically into account predominantly the nonadiabatic effects of the rotational inertia of the electrons [10]. The two nonadiabatic effects may be considered to arise from interactions between electronic states induced by the vibrational and rotational motions of the nuclei respectively. Although the fact that the centre of mass of the molecule fails to coincide with the centre of mass of the nuclei tends to blur and to mix the physical nature of the effects corresponding to the latter radial functions, the approximate description of these functions as rotational nonadiabatic or collectively vibrational nonadiabatic and adiabatic remains qualitatively useful. Defined according to eq. (1), all coefficients c, $g_j^{a,b}$ and $h_j^{a,b}$ are formally independent of mass, and dimensionless (except c_0 and $h_j^{a,b}$). As a consequence of the various contributions to the effective potential energy, the vibration-rotational terms consist also of several contributions; the expression for these terms is an extension of Dunham's form [13]:

$$E_{\nu J} = \sum_{k=0}^{N} \sum_{l=0}^{N} (Y_{kl} + Z_{kl}^{h,a} + Z_{kl}^{h,b} + Z_{kl}^{g,a} + Z_{kl}^{g,b})$$
$$\times (\nu + \frac{1}{2})^{k} (J^{2} + J)^{l}, \qquad (3)$$

in this equation in which the explicit isotopic dependence of E_{vJ} and the coefficients Y_{kl} and Z_{kl} has been suppressed to simplify the notation, the coefficients Y_{kl} are supposed to result from purely the internuclear potential energy V(z) and the centrifugal motion of the nuclei and associated electrons; the remaining coefficients, the four components of Z_{kl} , reflect respectively the obviously corresponding terms considered as perturbations separately additive in the effective potential energy according to eq. (1). Analytic expressions of the coefficients Y_{kl} as functions of the harmonic vibrational coefficient $k_{\rm e}$ (implicitly contained within $U_{1,0}$ or ω_e), the equilibrium separation R_e (implicitly contained within $U_{0,1}$ or B_e), the reduced mass μ and the potential-energy coefficients c_i have been published in machine-readable form complete up to j=10 [14]; further expressions containing coefficients up to j=20 have been generated according to hypervirial perturbation theory [15]. The coefficient c_0 in eq. (1) is defined in terms either of $U_{1,0}$ and $U_{0,1}$, $c_0 = U_{1,0}^2 / 4U_{0,1}$, or equivalently of k_e and R_e , $c_0 = k_e R_e^2/2ch$; the fundamental physical constants c and h enter these relationships because E_{uJ} , Y_{kl} and Z_{kl} are all expressed in wavenumber units for spectral applications. Hence of the five parameters $U_{1,0}$, $U_{0,1}$, c_0 , k_e and R_e , all formally independent of mass, only two are independent; in the actual analysis $U_{1,0}$ and $U_{0,1}$ are determined directly and the others are subsequently derived therefrom. Each term coefficient Y_{kl} and Z_{kl} consists of contributions in series,

$$Y_{kl} = Y_{kl}^{(0)} + Y_{kl}^{(2)} + Y_{kl}^{(4)} + \dots,$$
(4)

$$Z_{kl} = Z_{kl}^{(0)} + Z_{kl}^{(2)} + \dots,$$
⁽⁵⁾

independently of the method of generation of the actual expressions of the coefficients (or of the notation used to distinguish the contributions). Because the leading contributions $Y_{kl}^{(0)}$ are expressed as a product with the reduced (atomic) mass $\mu = M_a M_b / (M_a + M_b)$,

$$Y_{kl}^{(0)} = U_{kl} \mu^{(k/2+l)} , \qquad (6)$$

the coefficients U_{kl} become formally independent of mass. Although we have generated some expressions of the contributions $Y_{kl}^{(6)}$ and $Y_{kl}^{(8)}$ containing coefficients c_j up to j=18, only the leading term $Y_{kl}^{(0)}$ and the first two corrections $Y_{kl}^{(2)}$ and $Y_{kl}^{(4)}$ are required because the effects of experimental error of wavenumber measurement greatly exceed the magnitudes of further corrections. Analogously, for each of the four components of Z_{kl} even the first correction $Z_{kl}^{(2)}$ is negligible for the present data; furthermore we cannot include consistently additional terms

without taking into account the interaction of the various effects. Each auxiliary set of coefficients Z_{kl} is a function of both the potential-energy coefficients c_i and the respective coefficients either g_i or h_i for nuclei of types a or b. The coefficients Y_{kl} depend on the parameters c_i in a highly nonlinear manner, whereas the coefficients Z_{kl} depend on the parameters g_i or h_i linearly but c_i nonlinearly. A few expressions of Z_{kl}^{h} in terms of c_{i} and h_{i} have been already published in a different but equivalent form [16], which are however readily converted to be consistent with the present definition according to eq. (1); a larger collection of expressions containing the coefficients h_i up to j = 10 will be published with the extended set of expressions of Y_{kl} . Likewise a few expressions for Z_{kl}^{g} in terms of c_{i} and g_{i} have been reported [10]; a larger collection containing g_i up to j=10 will also be published in machine-readable form.

We apply the method of estimation of nonlinear parameters to determine the applicable coefficients $c_i, g_i^{a,b}$ and $h_i^{a,b}$ directly from the wavenumbers $\tilde{\nu}$ of only the vibration-rotational transitions because for these metal hydride species no pure rotational transitions have been measured. The wavenumbers $\tilde{\nu}$ of the transitions are the difference of the two terms E_{uJ} of the combining states; the criterion of convergence of a fit to a particular model is that the sum of the squares of the residuals between the measured and calculated values, $\tilde{v}_{obs} - \tilde{v}_{calc}$, is a minimum, hopefully the global minimum (apart from possibly the united atom). The algorithm of the fitting process employs the analytic expressions of not only the term coefficients Y_{kl} and the various components of Z_{kl} but also the first (partial) derivatives of Y_{kl} and the Z_{kl} with respect to the parameters, for instance ∂Y_{kl} ∂c_i , $\partial Y_{kl}/\partial U_{1,0}$ and $\partial Z_{kl}/\partial g_i$. The analytic expressions of the former derivatives up to j=10 have been already published in machine-readable form [14]; expressions of further derivatives of Y_{kl} and of the derivatives $\partial Z_{kl}^{g}/\partial g_{j}$ and $\partial Z_{kl}^{h}/\partial h_{j}$ will form part of the large collection to be published subsequently. The various dependences of the residuals on the masses $M_{\rm a}, M_{\rm b}$ and J make possible the determination of the coefficients g_i^a, g_i^b, h_i^a and h_i^b . Among various models tested during the fitting procedure, involving varied numbers of coefficients in the prospective five functions, we employ the F value as the criterion of selection; this statistic takes into account both the number of degrees of freedom (number of data minus the number of fitting parameters) and the standard deviation of the fit. All uncertainties in the tables represent one estimated standard error, and the uncertainties in k_e and R_e take into account also the error in the pertinent fundamental constants [17]. The atomic masses are from the latest consistent set [18].

3. Results

3.1. AgH

The 102 spectral transitions available number 41 for AgH [5] and 61 for AgD [9] within the ranges $0 \le v \le 3$ and $0 \le J \le 24$, in either case almost evenly divided between species containing ¹⁰⁷Ag and ¹⁰⁹Ag. The best fit, characterized by a standard deviation 0.078 m^{-1} , yielded the values of 15 independent parameters that were determined significantly, presented in table 1. Only three residuals exceeded two standard deviations, and then only marginally. The standard deviation of the alleged 104 transitions [9] was 0.08 m^{-1} , and the parameters U_{kl} and Δ_{kl} of that fit numbered 16. Urban et al. [9] found two of the latter parameters, namely $\mathcal{A}_{2,0}^{H}$ and $\mathcal{A}_{3,0}^{H}$, to assume magnitudes much greater than unity, specifically $|-12.92|\pm 0.16$ and $|-2065|\pm 37$, respectively.

3.2. GaH

The 208 spectral transitions available number 113 for GaH [6] and 95 for GaD [9] within the ranges $0 \le v \le 5$ and $9 \le J \le 29$, in either case almost evenly divided between species containing ⁶⁹Ga and ⁷¹Ga. The best fit, characterized by a standard deviation 0.075 m^{-1} , yielded the values of 16 independent parameters that were determined significantly, presented in table 2. Only one line had a residual greater than three standard deviations, and then only slightly greater; for this reason all lines were given equal weighting in the fitting process. The standard deviation of the fit of 210 transitions [9] to parameters of type U_{kl} and Δ_{kl} was 0.14 m⁻¹, almost twice as large as of our fit, even though their parameters numbered 18. All the reported values [9] of the parameters Δ_{kl} were of order unity, except $\Delta_{0,2}^H$ which was -14.55 ± 0.52 ; as one expects the value $\Delta_{0,2}^{H}\approx-11.9$ according to the approximate relation [19]

$$\Delta_{0,2} \approx 3\Delta_{0,1} - 2\Delta_{1,0} , \qquad (7)$$

the agreement is reasonable.

3.3. InH

The 162 spectral transitions available numbered 82 for InH [7] and 80 for InD [9] within the ranges $0 \le v \le 5$ and $0 \le J \le 34$, in this case with about twice as many lines for ¹¹⁵In species than for ¹¹³In species because of the relative natural abundance. The prod-

Table 1

Coefficients of the radial functions and other molecular properties of AgH X 12, all independent of mass

j	Cj	g ^{Ag}	g_j^{H}	h_j^{Ag} (10 ⁶ m ⁻¹)	$h_j^{\rm H}$ (10 ⁶ m ⁻¹)
0	$12011979.4 \pm 92 \text{ m}^{-1}$				
1	-1.425439 ± 0.000091	678.3 ± 128	-8.49 ± 1.76	-	-1.36 ± 0.35
2	0.92809 ± 0.00046	-	5.79 ± 1.91	_	-8.42 ± 1.13
3	-0.6107 ± 0.0033				62.9±10.6
4	0.4178 ± 0.022				-183.8 ± 43
5	-1.462 ± 0.050				
6	4.074 ± 0.160				
$U_{1,0} = U_{0,1} = k_e = 18$ $R_e = (1)$ range:	$175913.62 \pm 0.22 \text{ m}^{-1} \text{ u}^{1/2}$ 644.0571 ± 0.0066 m ⁻¹ u 12.32636 ± 0.00048 N m ⁻¹ 1.6178420 ± 0.0000083) × 10 ⁻¹⁰ m 1.33 < R/10 ⁻¹⁰ m < 2.11				

j	C _j	g _j Ga	g _j ^H	h_j^{Ga} (10 ⁶ m ⁻¹)	$h_j^{\rm H} \ (10^6 {\rm m}^{-1})$
0	$10463438.13 \pm 1.18 \text{ m}^{-1}$				
1	-1.347538 ± 0.000026	-	4.361 ± 0.047	-	-43.920 ± 0.051
2	1.038443 ± 0.000154	-	-9.88 ± 0.23	-	100.136 ± 0.149
3	-0.52152 ± 0.00079				-126.64 ± 1.03
4	0.0544 ± 0.0046				112.1 ± 4.5
5	-0.1829 ± 0.0190				
6	0.330 ± 0.042				
7	0.33 ± 0.23				
8	-3.33 ± 0.78				
$U_{1,0} =$	$159996.425 \pm 0.135 \text{ m}^{-1} \text{ u}^{1/2}$				
$U_{0,1} =$	611.62630±0.00110 m ⁻¹ u				
$k_{e} = 15$	$50.82422 \pm 0.00027 \text{ N m}^{-1}$				
$R_e = 1$	$.6601801 \pm 0.0000021$) $\times 10^{-10}$ m				
range:	$1.31 < R/10^{-10} \text{ m} < 2.36$				

Table 2 Coefficients of the radial functions and other molecular properties of GaH X $^{1}\Sigma$, all independent of mass

uct of the best fit, characterized by a standard deviation 0.177 m^{-1} , was the values of 15 independent parameters that were determined significantly, presented in table 3. Only five lines had residuals greater – but all much greater – than two standard deviations, all for In¹H and of those only one for ¹¹⁵In¹H; all these lines were assigned a weight one percent of that of the remaining lines so that their presence scarcely affected the outcome of the fit. As the residual of at least one of the latter five lines, namely $P_0(27)$ of ¹¹³In¹H nominally at 107980.08 m⁻¹, exceeded seven standard deviations, one must consider at least that line an outlier in a statistical sense,

due to a typographical or transcription error if not an error of assignment or measurement, although the residual from the reported fit to the coefficients Y_{kl} was not anomalously large [7]. The other four suspect lines are $R_1(6)$ of ¹¹⁵In¹H at 148655.70 m⁻¹ and of ¹¹³In¹H P₁(14) at 122102.46, $R_2(4)$ at 137277.54 and $R_3(19)$ at 140267.14 m⁻¹. We found all lines of In²H to fit within 1.5 standard deviations. The standard deviation of the weighted fit decreased to 0.125 m⁻¹. The standard deviation of the reported fit [9] of the same 162 spectral lines to 16 parameters of type U_{kl} and Δ_{kl} was 0.17 m⁻¹.

Table 3 Coefficients of the radial functions and other molecular properties of InH X Σ , all independent of mass

j	C _j	g_j^{\ln}	g_j^{H}	$h_j^{\rm In}~(10^6{ m m}^{-1})$	$h_j^{\rm H} \ (10^6 { m m}^{-1})$
0	$10888491.6 \pm 76 \text{ m}^{-1}$				
1	-1.429671 ± 0.000055	-	3.829±0.170	-	-38.432 ± 0.198
2	1.13147 ± 0.00026	-	-8.73 ± 0.88	-	91.70±0.62
3	-0.58012 ± 0.00099				-117.6 ± 3.8
4	-0.0285 ± 0.0056				92.7±16.6
5	-0.2329 ± 0.0159				
6	1.788 ± 0.041				
$U_{1,0} = U_{0,1} = k_e = 12$ $R_e = (1, 1, 2, 2, 3, 4, 3, 4, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5, 5,$	$147585.944 \pm 0.121 \text{ m}^{-1} \text{ u}^{1/2}$ $500.1063 \pm 0.0043 \text{ m}^{-1} \text{ u}$ $28.33364 \pm 0.00022 \text{ N m}^{-1}$ $1.8359766 \pm 0.0000081) \times 10^{-10} \text{ m}$ $1.47 < R/10^{-10} \text{ m} < 2.56$				

3.4. TlH

The 140 spectral transitions available number 94 for TlH [5] and 46 for TlD [9] within the ranges $0 \le v \le 3$ and $0 \le J \le 33$, in either case almost evenly divided between species containing ²⁰³Tl and ²⁰⁴Tl. The best fit, characterized by a standard deviation 0.185 m^{-1} , yielded values of 16 independent parameters significantly determined, presented in table 4. For two lines, $R_0(22)$ of each of ²⁰⁵Tl¹H at 147696.00 m⁻¹ and of ²⁰³Tl ¹H at 147699.40 m⁻¹, the residuals exceeded six standard deviations whereas for only one other line the residual exceeded (marginally) 1.5 standard deviations; for this reason the two lines assigned [8] as $R_0(22)$ are considered outliers, and their assignments or measurements suspect. When these two lines were accorded weights four percent of the remaining lines the standard deviation of the fit decreased to 0.14 m^{-1} . The standard deviation of 141 transitions [9] was 0.15 m^{-1} , and the parameters U_{kl} and Δ_{kl} of that fit numbered 16. Urban et al. [9] found two of the latter parameters, namely $\Delta_{2,0}^{H}$ and $\Delta_{3,0}^{H}$, to assume magnitudes much greater than unity, specifically $|-16.41| \pm 0.36$ and $|-600| \pm 17$ respectively.

4. Discussion

For each of these four metal hydride species, the standard deviation of the weighted fit was smaller,

and generally fewer independent parameters were required, than in the corresponding fits to sets of different parameters by Urban et al. [9]. Therefore on the basis of the content of the four tables and this comparison with the results of Urban et al. [9], the representation of the data in the form of the radial functions is clearly more precise in terms of the reproduction of the measured wavenumbers and more economical in terms of the number of independent parameters [1]. In agreement with Urban et al. who determined no values of the spectral parameters Δ_{kl}^{M} for the metal atoms, we failed to determine any values of the corresponding radial coefficients $h_i^{\rm M}$. For only one molecular species, AgH, we determined one value of the rotational nonadiabatic coefficient $g_{\perp}^{\rm M}$ of the metal atom; in that case the relatively large magnitude reflects its quotient with the mass of the silver atom, so that the relative contribution to the term values according to eq. (3) remains small. In each case four values of the radial coefficients $h_i^{\rm H}$ were determined significantly, and the magnitudes were invariably in the expected range, 10^6 — 10^9 ; the latter value is comparable with c_0 , as would be expected on the basis of the function for the effective potential energy in eq. (1) and as compared with values for other molecules [2-4]. In contrast some magnitudes of Δ_{kl}^{H} determined by Urban et al. [9] were anomalously large, as mentioned in the specific cases. The inability to determine values of either $h_i^{\mathbf{M}}$ or $\Delta_{kl}^{\mathbf{M}}$ from the data in only the mid-infrared spectral region indicates that the greater relative ac-

Table 4 Coefficient of the radial functions and other molecular properties of TIH X $^{1}\Sigma$, all independent of mass

j	\mathcal{C}_j	g_j^{T1}	g_j^{H}	$h_j^{\rm T1}$ (10 ⁶ m ⁻¹)	$h_j^{\rm H}$ (10 ⁶ m ⁻¹)
0	$10095913.9 \pm 23.3 \text{ m}^{-1}$				
1	-1.427153 ± 0.000148	_	0.352 ± 0.25	-	-33.171 ± 0.162
2	1.23777 ± 0.00086	-	75.9 ± 2.9	-	76.46 ± 0.50
3	-0.9948 ± 0.0025		-200.5 ± 9.1		-358.5 ± 7.8
4	0.1818 ± 0.027		588.4 ± 37		1291.7±37
5	0.0498 ± 0.112				
6	0.689 ± 0.26				
$U_{1,0} = U_{0,1} = k_e = 1$ $R_e = (range)$	$139460.66 \pm 0.32 \text{ m}^{-1} \text{ u}^{1/2}$ $481.6126 \pm 0.0033 \text{ m}^{-1} \text{ u}$ $14.59192 \pm 0.00053 \text{ N} \text{ m}^{-1}$ $1.8708948 \pm 0.0000066) \times 10^{-10} \text{ m}$ $: 1.55 < R/10^{-10} \text{ m} < 2.42$				

curacy of measurement of frequency or wavenumber of pure rotational transitions in the millimeter-wave range would be required for this purpose, as has been previously demonstrated [3,4]. The correlation coefficients of the parameters of each molecule (not presented here), derived from the variance-covariance matrix, included only a few values having magnitudes exceeding 0.95; typically such values were found connecting the parameters $h_1^{\rm H}$ and $h_2^{\rm H}$ and connecting $h_3^{\rm H}$ and $h_4^{\rm H}$, but not consistently elsewhere. Both the tolerable values of the correlation coefficients and the relatively small standard errors of the parameters, presented in the tables, indicate the goodness of the fits.

Comparison of the potential-energy coefficients among the four species indicates the existence of possible trends, such as the values of $-c_1 \approx 1.4$, $c_2 \approx 1.05, -c_3 \approx 0.6$ etc. The apparent constancy of $-c_1 \approx 1.427 \pm 0.002$ for the three hydrides other than InH is remarkable. In all cases the magnitudes of the coefficients remain about unity or less, except possibly that of the last coefficient which is larger. Although transitions to vibrational states up to v=5were measured for both GaH and InH, for only the former molecule was it practicable to determine potential energy coefficients beyond c_6 . The potential energy and other radial functions are defined within a range of internuclear distance corresponding to approximately the classical turning points of the highest vibrational state for which spectral data were included in the fit; this range of each molecule is specified in the corresponding table of results. If one, taking advantage of the well behaved nature of the argument z as $R \rightarrow \infty$ [11], applies the conditions [20] to take account of the limiting dependence of the potential energy at large separations R, one can accordingly extend the range of validity of the potential-energy functions; by this means one would be able to predict, at least approximately, the wavenumbers of spectral transitions well beyond the measured ranges used for the generation of the parameters in the four tables. The equilibrium internuclear distance of each molecule has been particularly well defined, having a relative precision of a few parts per million.

Acknowledgement

I thank Mr. C.C. Ho and Mr. S.F. Chuang for assistance in the computations and the National Science Council of the Republic of China for financial support.

References

- [1] J.F. Ogilvie, Spectrochim. Acta 46A (1990) 43.
- [2] J.F. Ogilvie, J. Mol. Spectry. 148 (1991) 243.
- [3] J.F. Ogilvie, Chem. Phys. Letters 183 (1991) 40.
- [4] J.F. Ogilvie and M.C.C. Ho, J. Mol. Struct. 263 (1991) 167.
- [5] H. Birk and H. Jones, Chem. Phys. Letters 161 (1988) 321.
- [6] R.D. Urban, U. Magg and H. Jones, Chem. Phys. Letters 154 (1989) 135.
- [7] A.H. Bahnmaier, R.D. Urban and H. Jones, Chem. Phys. Letters 155 (1989) 269.
- [8] R.D. Urban, A.H. Bahnmaier, U. Magg and H. Jones, Chem. Phys. Letters 158 (1989) 443.
- [9] R.D. Urban, H. Birk, P. Polomsky and H. Jones, J. Chem. Phys. 94 (1991) 2523.
- [10] J.F. Ogilvie, to be published.
- [11] J.F. Ogilvie, Proc. Roy. Soc. A 378 (1981) 287; A 381 (1982) 479.
- [12] J.F. Ogilvie, J. Chem. Phys. 88 (1988) 2804.
- [13] J.L. Dunham, Phys. Rev. 41 (1932) 721.
- [14] J.F. Ogilvie, Computer Phys. Commun. 30 (1983) 101.
- [15] F.M. Fernandez and J.F. Ogilvie, Phys. Rev. A 42 (1990) 4001.
- [16] J.F. Ogilvie, Chem. Phys. Letters 140 (1987) 506
- [17] E.R. Cohen and B.N. Taylor, Rev. Mod. Phys. 59 (1987) 1121.
- [18] A.H. Wapstra and G. Audi, Nucl. Phys. A 432 (1985) 1.
- [19] J.F. Ogilvie, Spectros. Letters 22 (1989) 477.
- [20] J.F. Ogilvie, J. Chem. Phys. 88 (1988) 2804.