Dunham Potential Energy Coefficients of the Hydrogen Halides and Carbon Monoxide

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The Dunham potential energy coefficients $a_i, 0 \le i \le 6$ (except 4 for HI) have been derived from spectroscopic data of hydrogen halides HF, HCl, HBr, and HI, and carbon monoxide in their ground electronic states. A full error analysis has produced standard deviations of both these a_i and further energy coefficients Y_{lj} . Comparison with experimental data shows good agreement; trends in the hydrogen halide series are discussed.

The two primary molecular properties of a diatomic molecule, which are massinvariant within the Born–Oppenheimer approximation, are the equilibrium bondlength R_e and force constant k_e . These two characteristic parameters are the principal determinants of the rotational and vibrational spectra, respectively. In reality, these parameters reflect only two aspects of the molecular vibrational potential function of the ground electronic states of the ¹ Σ diatomic molecules to be considered here. Although there are many model potential functions which can be fit to these two, and other, parameters derived from vibration–rotational spectra, for the lower portion of the spectroscopic parameters, and thus the energy levels within the approximation of the fitting procedures by which the spectroscopic parameters are derived, is still the Dunham potential function (1):

$$V/hc = a_0 x^2 (1 + \sum_{i=1}^{n} a_i x^i), \quad V = 0 \text{ at } R = R_e.$$

Here x is a reduced internuclear separation,

$$x = (R - R_{\rm e})/R_{\rm e},$$

and R is the instantaneous internuclear separation; a_0 is related to the equilibrium force constant according to the equations

$$a_0 = \frac{\omega_{\rm e}^{*2}}{4B_{\rm e}^*} = \frac{k_{\rm e}R_{\rm e}^2}{2hc} = \frac{B_{\rm e}^*}{\gamma^2},$$

where $(d^2V/dR^2)_{R=Re} = k_e$. The other Dunham potential coefficients a_i , $i \ge 1$, have no particular physical interpretation, but their values obviously determine the manner in which the lower portion of the potential function, $V \le \frac{1}{2}\mathfrak{D}_e$ (where \mathfrak{D}_e is the depth

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of the potential well), deviates from the parabolic form of the limiting case, $a_i = 0$ for all $i \ge 1$, of the harmonic oscillator. The harmonic oscillator is really a poor approximation to a molecular vibrator, as can be demonstrated by the fact that the magnitudes of a_i can greatly exceed unity, as well as by the asymptotic approach to the dissociation limit when $R \gg R_c$.

For only a few diatomic molecules have the coefficients a_i , $i \ge 3$, been determined at all, and even in these few cases the accuracy of determination has not been well assessed. We report here our results, based on an error analysis including error propagation, for the four hydrogen halides and carbon monoxide for which spectroscopic data, of variable accuracy, are available. The potential coefficients may in turn be used in determination of other molecular properties such as dipole-moment functions (2), or to test spectroscopic parameters of isotopic molecules.

METHOD

We have determined potential coefficients a_i , i < 7, by an iterative procedure from equations given by Dunham (1), using coefficients Y_{10} , Y_{20} , Y_{30} , Y_{40} , Y_{01} , Y_{11} , Y_{21} , and Y_{31} in the energy level equation

$$E_{vJ} = \sum_{l, j=0} Y_{lj} (v + \frac{1}{2})^l [J(J+1)]^j.$$

For HF (3), HCl (4), and CO (5), all these coefficients are available directly. For HBr the purely vibrational coefficients Y_{10} , Y_{20} , Y_{30} , and Y_{40} were newly derived using the recent spectroscopic data of Bernage *et al.* (6); older rotational parameters were used (7). Our derived Y_{i0} are given in Table I. For HI (8), because no value of Y_{31} is yet available, only a_{i} , $i \leq 4$, could be determined.

In each iteration, all values of calculable a_i were adjusted, as well as the Dunham B_e and ω_e (denoted here by B_e^* and ω_e^*), where Dunham corrections to Y_{01} and Y_{10} were applied. Fifteen significant figures were required to be carried through all arithmetic to ensure full accuracy of results within experimental errors of the Y_{lj} . After self-consistency and stable convergence had been achieved, values of standard deviations of the Y_{lj} used were employed to conduct a realistic assessment of the a_i by the error propagation method of multivariate error analysis (9). These results, a_i , B_e^* , ω_e^* and their estimated standard deviations, are presented in Table II. These a_i reproduced the initial Y_{lj} very satisfactorily.

For some molecules, further Y_{lj} , in the collection Y_{02} , Y_{12} , Y_{22} , Y_{03} , Y_{13} , and Y_{04} are available. But generally the nominal experimental accuracy with which these are determined is appreciably inferior to that of the other previously specified Y_{lj} because of the relatively small magnitudes of these quantities. However, these further Y_{lj} are

Table I. Vibrational energy coefficients of HBr

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Y_{10} = 264920.17 \text{ m}^{-1}

Y_{20} = -4544.07 \text{ m}^{-1}

Y_{30} = 8.1383 \text{ m}^{-1}

Y_{40} = -1.07583 \text{ m}^{-1}
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I. Dunham potential energy coefficients and other parameters of the potential

	HF	HC1	HBr	HI	CO
a ₀ /m ⁻¹	20434850	21112870	20729530	20467550	60945188
	±1200	±150	±210	±670	±4
^a 1	-2,2538	-2.364256	-2.437284	-2.5326	-2.6971840
	±16x10 ⁻⁴	±16x10 ⁻⁵	±25x10 ⁻⁵	±15x10 ⁻⁴	±70x10 ⁻⁷
^a 2	3.4882	3.66285	3.84581	3.9587	4.506468
	±88x10 ⁻⁴	±12x10 ⁻⁴	±18x10 ⁻⁴	±0.017	±45x10 ⁻⁶
a ₃	-4.4986	-4.7063	-5.0447	-5.493	-5.97219
	±0.035	±99x10 ⁻⁴	±0.010	±0.085	±20x10 ⁻⁵
a ₄	4.704	5.2126	5.4451	9.602	7.0507
	±0.17	±0.080	±0.075	±0.33	±13×10 ⁻⁴
a ₅	-2.91 ±0.74	-5.5226 ±0.43	-4.635 ±0.45	-	-7.6768 ±10x10 ⁻³
^a 6	-1.76 ±2.86	8.356 ±2.5	5.584 ±2.3	•	6.551 ±0.094
ω _e /m ⁻¹	413876.7	299105.98	264934.85	230887.1	216981.49
	±7.5	±0.88	±1.3	±1.2	±0.008
B [*] _e /m ⁻¹	2095.61	1059.3586	846.5034	651.139	193.12832
	±0.09	±31x10 ⁻⁴	±25x10 ⁻⁴	±0.020	±4x10 ⁻⁶
Ŷ	1.0126735x10 ⁻²	7.08350x10 ⁻³	6.390276x10 ⁻³	5.64032x10 ⁻³	1.78013636x10 ⁻³
	±48x10 ⁻⁸	±3x10 ⁻⁸	±4x10 ⁻⁸	±18x10 ⁻⁸	±7x10 ⁻¹¹
k _e /N m ⁻¹	965.909	516.360	411.666	314.055	1901.8951
	±0.04	±0.003	±0.004	±0.003	±1x10 ⁻⁴
R _e /10 ⁻¹² m	91.680	127.4542	141.4423	160.9113	112.83225
	±0.002	±2x10 ⁻⁴	±2x10 ⁻⁴	±2x10 ⁻³	±1×10 ^{~6}
v_{e}/m^{-1}	4938000	3756000	3193000	2609000	9054180
	±6000	±1000	±2000	±6000	±1000

function of some diatomic molecules in their ${}^{1}\Sigma$ ground electronic states

calculable from the a_i , i < 4, and B_e^* and ω_e^* , so experimental and calculated values may be compared as a further test of the a_i . Where these further Y_{lj} are not available, the calculated values represent predictions which may be helpful in future spectroscopic analyses. These results are presented in Table III, including a comparison with experimental results where possible. All results are given in strict SI units, and the quoted uncertainties represent one standard deviation.

DISCUSSION

Where previous sets of a_i and estimates of their accuracy exist, the present results are in good agreement. Small discrepancies can be attributed either to the different spectroscopic data used here (in some cases) or to our improved computational method.

The error estimates of the a_i reflect well the accuracy of the original spectroscopic data. Thus the spectroscopic parameters of CO obtained from laser emission measurements (5) are far more accurate than those for hydrogen halides, and standard deviations of the potential coefficients of CO are accordingly better defined, by at least a factor of 20; even a_6 is very significant, unlike values of a_6 (a_4 for HI) for the other molecules.

Correlation matrices for the potential coefficients a_i , B_e^* , and ω_e^* in one case, and for the calculated energy coefficients Y_{lj} in the other case, were also computed for each

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		HF	HC1	HBr	HI	CO
۲ ₀₀	(calc.)	413 ±10	159.77 ±0.63	120.82 ±0.76	53.02 ±5.2	19.035 ±5x10 ⁻³
ү ₀₂	(calc.)	-2.1497x10 ⁻¹ ±3x10 ⁻⁵	-5.31582x10 ⁻² ±5x10 ⁻⁷	-3.45722x10 ⁻² ±4x10 ⁻⁷	-2.0708x10 ⁻² +2x10 ⁻⁶	-6.1200x10 ⁻⁴ ±6.0x10 ⁻¹¹
	(obs.)	-2.151x10 ⁻¹ ±4x10 ⁻⁴	-5.31936x10 ⁻² ±1x10 ⁻⁶	-3.4575x10 ⁻² ±1.1x10 ⁻⁵	-2.07x10 ⁻² ±4x10 ⁻⁴	-6.1215x10 ⁻⁴ ±2.9x10 ⁻⁸
^Y 12	(calc.) (obs.)	6.133x10 ⁻³ ±6x10 ⁻⁵ 6.8×10 ⁻³	7.207×10 ⁻⁴ ±1.7×10 ⁻⁶ 7.510×10 ⁻⁴	3.602x10 ⁻⁴ ±1.5x10 ⁻⁶ 3.97x10 ⁻⁴	4.64x10 ⁻⁵ ±8.7x10 ⁻⁶	1.04457x10 ⁻⁷ ±1.4x10 ⁻¹⁰ 1.1526x10 ⁻⁷
		±4x10 ⁻⁴	±1x10 ⁻⁶	±6.3x10 ⁻⁰		±2x10 ⁻⁹
Υ ₂₂	(calc.)	-2.718x10 ⁻⁴ +2.7x10 ⁻⁵	-2.594×10 ⁻⁵ ±1.7×10 ⁻⁶ _	-2.858x10 ⁻⁵ ±1.4x10 ⁻⁶	5.5x10 ⁻⁶ ±1.1x10 ⁻⁶	-1.7535x10 ⁻⁸ ±4.0x10 ⁻¹¹
	(obs.)	-2.9x10 ⁻⁴ ±5x10 ⁻⁵	-4.00x10 ⁻⁵ ±1.0x10 ⁻⁷	-3.8x10 ⁻⁵ ±2.8x10 ⁻⁶	-	-1.805x10 ⁻⁸ ±1.5x10 ⁻¹⁰
۲ ₀₃	(calc.)	1.6445x10 ⁻⁵ ±3.4x1′0 ⁻⁸	1.69558x10 ⁻⁶ ±4.3x10 ⁻¹⁰	7.9432x10 ⁻⁷ ±3.6x10 ⁻¹⁰	3.0802x10 ⁻⁷ ±9.6x10 ⁻¹⁰	5.8727x10 ⁻¹⁰ ±1.4x10 ⁻¹⁴
	(obs.)	1.57x10 ⁻⁵ ±1.7x10 ⁻⁶	1.740x10 ⁻⁶ ±1x10 ⁻⁸	7.63x10 ⁻⁷ ±1.6x10 ⁻⁸	-	5.8272x10 ⁻¹⁰ ±6x10 ⁻¹²
۲ ₁₃	(calc.)	-3.12x10 ⁻⁷ ±4.6x10 ⁻⁸	-4.052x10 ⁻⁸ ±1.8x10 ⁻⁹	-2.564x10 ⁻⁸ ±7.1x10 ⁻¹⁰	-3.34x10 ⁻⁸ ±1.1x10 ⁻⁹	-1.4428x10 ⁻¹¹ ±1.9x10 ⁻¹⁵
	(obs.)	-	-6.34x10 ⁻⁸ ±1x10 ⁻⁹	-5.5x10 ⁻⁸ ±6x10 ⁻⁹	-	-1.738x10 ⁻¹¹ ±2.3x10 ⁻¹³
Y ₀₄	(calc.)	-1.484x10 ⁻⁹	-8,507x10 ⁻¹¹	-3.3688x10 ⁻¹¹	-1.4247x10 ⁻¹¹	-3.6086x10 ⁻¹⁵
04		±1.6x10 ⁻¹¹	±1.3x10 ⁻¹³	±7.7x10 ⁻¹⁴	±2.9x10 ⁻¹³	±1.6x10 ⁻¹⁹
	(obs.)	-	-9.93x10 ⁻¹¹ ±1x10 ⁻¹²	-	-	-

Table III. Calculated and observed values of energy coefficients $Y_{\xi\,j}$ of some diatomic molecules in their $^{1}\Sigma$ ground electronic states $(m^{-1} \text{ units})$

molecule. The general nature of elements of the correlation matrices in the separate sets was similar for all these molecules. In general the potential coefficients a_i were not strongly correlated with each other and ω_e^* and B_e^* (absolute values of off-diagonal elements less than 0.9) except that a_1 was always fairly strongly anticorrelated with a_2 (matrix element, ≤ -0.95). The calculated energy coefficients Y_{lj} were generally not appreciably correlated with each other except Y_{04} and Y_{12} , for which the matrix element was ~ 0.99 ; the reason for this seems to be the similar functional dependence of Y_{04} and Y_{12} on a_1 and a_2 (1). In deriving correlation matrices for the potential coefficients a_i we assumed in each case except CO that the input spectroscopic data were independent or uncorrelated; correlation matrices for the spectroscopic data are lacking except for CO (5). When the correlation matrices for the spectroscopic data of CO were not included in the error analysis, the effect, in most cases, was to increase the standard deviation of both the predicted Y_{ij} and the potential coefficients by (12 ± 3) percent. Because this effect is practically negligible, we conclude that the stated uncertainties in the corresponding quantities of the hydrogen halides, for the spectroscopic data of which the correlation matrices are unavailable, tend to constitute upper limits of the true uncertainties. In the production of correlation matrices for calculated energy coefficients Y_{ij} , however, correlation matrices for the potential coefficients a_i were properly used (9).

The calculated energy coefficients Y_{lj} are generally in good agreement with observed values within experimental error. Because these Y_{lj} are higher-order spectroscopic

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parameters, procedures of fitting experimental term values to finite power series tend to make these Y_{lj} more sensitive to the extent of truncation of the series than lower-order Y_{lj} . Least-squares-fitting procedures have customarily been used to generate these Y_{lj} , but even inclusion of weighting factors in the analysis leaves the derived coefficients prone to variation depending on the nature of the arguments in the power series (10). On the theoretical side, further correction terms in Dunham's theory would have a finite effect on the calculated Y_{lj} , but these corrections are in general expected to be smaller than the standard deviations due to error in a_{ij} , except possibly in the case of CO.

Certain trends may be noted for the hydrogen halide molecules. Although a_0 varies remarkably little in this group, the other well-defined potential coefficients a_1-a_4 (except a_4 of HI, which is suspect) show a smooth monotonic increase as the halogen mass increases. This effect seems consistent with the generalization of relative constancy of a_1 and a_2 for hydrides (11, 12), about -2.4 ± 0.1 and 3.8 ± 0.2 , respectively. The potential coefficients of HI are generally closer to those of CO than of HF, but perhaps CO is the exceptional molecule in this case because the average values of a_1 and a_2 for strongly bound nonhydrides (11, 12), -3.2 ± 0.1 and 6.4 ± 0.75 , respectively, are significantly larger than those of CO. For convenience, certain other properties of the potential function, including the equilibrium separation R_e , force constant k_e , and depth \mathfrak{D}_e of the potential well, are also collected in Table II; the latter parameter \mathfrak{D}_e cannot be obtained directly from the vibration-rotational parameters of the lower region of the potential well, but it has been estimated from thermochemical data (13) except for HF (14) and CO (15) where it has been deduced directly from spectroscopic measurements.

ACKNOWLEDGMENTS

We are grateful to Dr. R. H. Tipping for helpful comments and to the National Research Council of Canada for financial support.

RECEIVED: November 28, 1975

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