Dunham Energy Parameters of Isotopic Carbon Monoxide, Hydrogen Halide, and Hydroxyl Radical Molecules

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Dunham potential energy coefficients a_1-a_6 for ¹²C¹⁶O, ¹³C¹⁶O, ¹³C¹⁶O, H⁸¹Br_. HI, and OH have been calculated, including error limits, from published experimental spectroscopic data. There is no indication of deviation from Born–Oppenheimer behavior for a_1-a_6 of the carbon monoxide molecules, and the mass-independent internuclear separation R_e and force constants k_e and a_0 have also been calculated.

Since the preparation of the previous article (1) on the Dunham potential energy parameters of the hydrogen halides (HF, H³⁵Cl, H⁸¹Br, HI) and carbon monoxide (¹²C¹⁶O), further experimental data from the vibration-rotational spectra of isotopic species of carbon monoxide (¹³C¹⁶O and ¹²C¹⁸O) (2, 3), hydrogen bromide (4), hydrogen iodide (5), and the hydroxyl radical (OH) (6) have become available. The former data are of interest because a test of the isotopic invariance of potential function parameters is thus possible for a nonhydride molecule for perhaps the first time. Also, carbon monoxide is the best characterized diatomic molecule from experimental spectroscopy in that the available spectroscopic parameters Y_{ij} are more abundant and more accurate than for any other molecule.

Within the Born-Oppenheimer approximation, the parameters defining the potential function should be mass invariant. Table I shows that the standard deviations of $a_1 - a_6$, reflecting the experimental inaccuracy of the $Y_{li}(\beta)$, are larger than the small differences between comparable quantities of the various isotopic molecules. (Treatment of results and notation follow previous practice (1).) For these spectroscopic parameters, one standard deviation (for each quantity, as employed in the error propagation analysis) was taken to be half the stated confidence intervals (3). For the other set of data on isotopic carbon monoxide (2), similar analysis revealed that the nominal standard deviations were smaller but that the differences between the a_i were slightly larger. The emission spectra (3) were much more extensive than the absorption spectra (2), so the Dunham potential parameters derived from the former are probably more reliable, although the actual differences between the resulting sets of a_i are within the precision derived from the experimental data. In contrast, the disagreement between the derived parameters a_0 , k_e , and R_e far exceeds the nominal standard deviations. More sophisticated methods for estimating the isotopically invariant internuclear separation and curvature at the minimum of the Born-Oppenheimer potential (7-9) exist. The most Comparison of Potential Energy Function Parameters of Isotopic Carbon Monoxide Molecules

	¹² c ¹⁶ 0	¹³ c ¹⁶ 0	¹² c ¹⁸ o
a ₀ / m ⁻¹	60945207 <u>+</u> 2	60944423 <u>+</u> 9	60944736 <u>+</u> 15
al	$-2.697174 \pm 1 \times 10^{-5}$	$-2.697119 \pm 7 \times 10^{-5}$	$-2.697183 \pm 2x10^{-4}$
^a 2	$4.50636 \pm 9 \times 10^{-5}$	4.50614 <u>+</u> 5x10 ⁻⁴	.50666 <u>+</u> 0.0011
a ₃	-5.97124 <u>+</u> 0.0009	-5.9710 ± 0.0032	-5.9731 ± 0.006
a4	7.0463 ± 0.0079	7.043 ± 0.024	7.046 <u>+</u> 0.04
a ₅	-7.672 <u>+</u> 0.047	-7.64 ± 0.13	-7.62 <u>+</u> 0.21
a ₆	6.59 <u>+</u> 0.27	6.49 <u>+</u> 0.63	6.39 <u>+</u> 0.96
R [★] _e / 10 ^{−12} m	112.83226 ± 6x10 ⁻⁶	112.83184 ± 1x10 ⁻⁵	$112.83180 \pm 2 \times 10^{-5}$
k_e^* / Nm^{-1}	1901.8956 <u>+</u> 0.0003	1901.8850 <u>+</u> 0.0005	1901.8964 <u>+</u> 0.001
ω_e^*/m^{-1}	216981.52 ± 0.01	212144.08 ± 0.04	211739.88 ± 0.02
B_{e}^{*} / m^{-1}	193.12832 <u>+</u> 2x10 ⁻⁵	$184.61538 \pm 4 \text{x} 10^{-5}$	183.9116 <u>+</u> 8x10 ⁻⁵

general method (9) yields the following results:

$$\begin{split} \mu B_e &= h(8\pi^2 c R_e^2)^{-1} = (2.1991696 \pm 4.5 \times 10^{-6}) \times 10^{-24} \text{ kg m}^{-1}; \\ \mu^{\frac{1}{2}} \omega_e &= k_e^{\frac{1}{2}} (2\pi c)^{-1} = (2.3151423 \pm 1 \times 10^{-6}) \times 10^{-8} \text{ kg}^{\frac{1}{2}} \text{ m}^{-1}; \\ (\mu^{\frac{1}{2}} \omega_e)^2 / 4\mu B_e &= 60\ 930\ 771 \pm 50\ \text{m}^{-1}; \end{split}$$

<u> </u>	HBr	HI	OH
a ₀ /m ⁻¹	20729060 ± 630	20471590 ± 370	18472000 ± 330
a _l	~2.43632 ± 0.00074	-2.55385 ± .00091	-2.2613 ± 0.0017
a_2	3.8430 ± 0.0067	4.0953 ± .0062	3.3977 ± 0.0096
a ₃	-5.0996 ± 0.046	-5.2398 ± .035	-4.254 ± 0.043
a ₄	5.78 ± 0.35	3.92 ± .25	4.49 ± 0.26
a ₅	-4.6 ± 2.1	2.8 ± 1.4	-3.9 ± 1.2
a ₆	0.08 ± 16	0.65 ± 6.9	4.7 ± 5.0
$\omega_{\mathbf{e}}^{\star}$ /m ⁻¹	264931.4 ± 4.7	230920.5 ± 2.8	373807.5 ± 7.2
B_e^{\star}/m^{-1}	846.5004 ± 0.0047	651.1986 ± .0043	1891.13 ± 0.11
γ	$6.390337 \times 10^{-3} \pm 1 \times 10^{-7}$	5.640023 ± 8x10 ⁻⁸	$1.011822 \pm 6 \times 10^{-7}$
k _e ∕N m ^{−l}	411.655 ± 0.011	314.146 ± 0.005	780.55 ± 0.06
R _e /10 ⁻¹² _{IR}	141.4425 ± 0.0004	160.9035 ± 0.0005	96.9645 + 0.0027
\mathcal{D}_{e}/m^{-1}	3193000 ± 2000	2609000 ± 6000	3734000 ± 8000

TABLE II Parameters of Dunham Potential Functions*

 $*\gamma = 5.640023 \times 10^{-3}$ for HI, 1.011822 $\times 10^{-2}$ for OH.

TABLE	ш
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Calculated and Observed Energy Coefficients Y_{lj} (m⁻¹ Units)

		HBr	ні	ОН
۲ ₀₀	(calc)	120.8 ± 2.7	71.0 ± 2.1	294.1 + 9.9
Y ₀₂	(calc)	-3.4571×10 ⁻² ±1.2×10 ⁻⁶	-2.0722×10 ⁻² ±6.3×10 ⁻⁷	-1,9365×10 ⁻¹ ±3.3×10 ⁻⁵
	(obs)	-3.4582×10 ⁻² ±2×10 ⁻⁵	-2.0673×10 ⁻² ±5×10 ⁻⁵	-1.9380×10 ⁻¹ ±4.2×10 ⁻⁴
Y ₁₂	(calc)	3.606×10 ⁻⁴ ±6.5×10 ⁻⁶	9.05×10 ⁻⁵ ±2.4×10 ⁻⁶	4.205×10 ⁻³ ±5.7×10 ⁻⁵
	(obs)	3.89×10 ⁻⁴ ±2×10 ⁻⁵	-	4.3198×10 ⁻³ ±3.6×10 ⁻⁶
¥ ₂₂	(calc)	-2.85×10 ⁻⁵ ±5.1×10 ⁻⁶	~3.26×10 ⁻⁵ ±1,6×10 ⁻⁶	-1.98×10 ⁻⁴ ±4.1×10 ⁻⁵
	(obs)	-3.7×10 ⁺⁵ ±2.4×10 ⁻⁵	-	-2.4165×10 ⁻⁴ =6.7×10 ⁻⁷
Y ₀₃	(calc)	7.957×10 ⁻⁷ ±1.1×10 ⁻⁹	2.9397×10 ⁻⁷ ±6.0×10 ⁻¹⁰	1.4641×10 ⁻⁵ ±3.4×10 ⁻⁸
	(obs)	7.67×10 ⁻⁷ ±4×10 ⁻⁸	-	1.421×10 ⁻⁵ ±6.8×10 ⁻⁷
Y ₁₃	(calc)	$-3.10 \times 10^{-8} \pm 3.5 \times 10^{-9}$	-9.75×10 ⁻¹⁰ ±9.7×10 ⁻¹⁰	-3.73×10 ⁻⁷ ±6.6×10 ⁻⁸
	(obs)	-5.15×10 ⁻⁸ ±3×10 ⁻⁸	-	-6.03×10 ⁻⁷ ±2.3×10 ⁻⁷
Y ₀₄	(calc)	-3.374×10 ⁻¹¹ :3×10 ⁻¹³	-1.274×10 ⁻¹¹ ±9×10 ⁻¹⁴	-1.534×10 ⁻⁹ ±1.6×10 ⁻¹¹
	(obs)	-	-	-

where μ is the atomic reduced mass. Therefore $R_e = (1.1282281 \pm 2 \times 10^{-6}) \times 10^{-10}$ m, $k_e = 1901.764 \pm 0.02$ N m⁻¹, and $a_0 = 60$ 930 771 \pm 50 m⁻¹. The mass coefficients for Y_{10} and Y_{01} are $\Delta_{10}{}^{\rm c} = 0.784 \pm 0.01$, $\Delta_{10}{}^{\rm o} = -0.051 \pm 0.015$, $\Delta_{01}{}^{\rm c} = -2.084 \pm 0.024$, and $\Delta_{01}{}^{\rm o} = -2.139 \pm 0.042$. The particular method of Watson (8) yields equivalent results for R_e . Thus the specified values represent the best estimates of the mass-independent magnitudes of these characteristic parameters for the ground electronic state of carbon monoxide.

For the hydrogen halides HstBr and HI, the new results in Tables II and III supersede those of the previous study (1), but a large set of these parameters has not previously been available for the hydroxyl radical. For HBr, the potential energy coefficients in Table II and the energy coefficients Y_{ij} in Table III have somewhat larger standard deviations than those obtained by Stocker and Goldman (10); however, because the experimental data (4) are a consistent set of larger size than before, the given data are to be preferred. The extended spectroscopic data for HI (5) permit estimation of a_5 and a_6 , but the precision is relatively poor. In particular, the positive sign of a_5 and small magnitude of a_6 seem anomalous, but the error limits may not make any deduction meaningful; these sign and magnitude effects are to be contrasted with the values $a_5 = -26 \pm 9$ and $a_6 = 74 \pm 37$ that are obtained from earlier spectra from the same laboratory (11). For the hydroxyl radical, which has a ²II ground state, any spin effects have been neglected in deriving the results in Tables II and III; it is notable that these results are very similar in magnitudes to those corresponding to hydrogen fluoride presented earlier (1).

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