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Robin S. McDowell

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# Rotational partition functions for linear molecules<sup>a)</sup>

Robin S. McDowell

University of California, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

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An accurate closed-form expression for the rotational partition function of linear polyatomic molecules in  $^1\Sigma$  electronic states is derived, including the effect of nuclear spin (significant at very low temperatures) and of quartic and sextic centrifugal distortion terms (significant at moderate and high temperatures). The proper first-order quantum correction to the classical rigid-rotator partition function is shown to yield  $Q_r \approx \beta^{-1} \exp(\beta/3)$ , where  $\beta \equiv hcB/kT$  and  $B$  is the rotational constant in  $\text{cm}^{-1}$ ; for  $\beta \geq 0.2$  additional power-series terms in  $\beta$  are necessary. Comparison between the results of this treatment and exact summations are made for HCN and  $\text{C}_2\text{H}_2$  at temperatures from 2 to 5000 K, including separate evaluation of the contributions of nuclear spin and centrifugal distortion.

## I. INTRODUCTION

Rotational partition functions have applications to the distribution of molecules among various rotational states and the intensities of vibration-rotation transitions in molecular spectra, and in the calculation of standard-state ideal-gas thermodynamic functions. The rotational partition function is simply the sum over the rotational states of a molecule,

$$Q_r = \sum_n g_n e^{-hcE_n/kT},$$

where  $E_n$  is the energy (in  $\text{cm}^{-1}$ ) of rotational level  $n$  with statistical weight  $g_n$ , and the sum is taken over all such levels.

Except at extremely low temperatures, or for molecules with very widely spaced rotational levels ( $\text{H}_2$  and isotopes), this expression converges too slowly for direct summation to be convenient. Instead, summation can be replaced by integration to yield a simple closed-form expression for  $Q_r$ , which, as a classical approximation, is valid at high temperatures. The discrete quantum nature of the rotational energy levels is usually accounted for with certain correction terms in the form of a power series in  $1/T$ . This procedure, which is equivalent to Euler-Maclaurin summation, results in useful expressions for the partition functions of the different symmetry classes of polyatomic molecules. Such formulas have been available since the late 1920's,<sup>1</sup> are widely used, and perform well at temperatures for which almost any molecule (except hydrogen) has a significant equilibrium vapor pressure.

There are several reasons, however, why it is appropriate to reexamine the available formulas for  $Q_r$ . These reasons apply to calculations at low, intermediate, and high temperatures:

(1) Adiabatic cooling techniques now allow the spectroscopic study of rotationally relaxed vapor-phase molecules at temperatures far below that at which condensation normally occurs. There are also astrophysical applications in which, because of very long absorbing paths, low-density species can be observed near the temperature of interstellar

space. Consequently there is new interest in accurate partition functions at temperatures low enough for quantum effects and nuclear spin to become significant, but still high enough for direct summation to be cumbersome. Even when summation is feasible, analytical expressions are usually quicker and more convenient, especially when the energy-level formula includes centrifugal distortion terms.

(2) With the increased availability of Doppler-limited and sub-Doppler spectroscopic resolution, individual vibration-rotation transitions can be resolved even for molecules with relatively large moments of inertia and hence closely spaced lines. Proper treatment of such data at any temperature requires that nuclear-spin statistics be rigorously included in the rotational partition function.

(3) Modern spectroscopic techniques are resulting in the better determination of molecular rotational constants, and the determination of higher order constants. The resulting improvement in the representation of rotational energy levels can yield more accurate partition functions at high temperatures. This is only possible, of course, if one has available the mathematical form of the corrections due to such effects as centrifugal distortion and possible level splitting.

Recently the rotational partition functions of spherical-top molecules were reexamined.<sup>2</sup> The existing, and widely used, closed-form expression for  $Q_r$  in this case provided an accuracy of 1% for  $\text{CH}_4$  at temperatures of 40 K and above. It was shown that the addition of two correction terms improved this to better than 0.01% for  $T \geq 10$  K. One of these corrections accounts for nuclear spin at low temperatures; the second includes the higher temperature influence of quartic and sextic centrifugal distortion terms, providing seven-place accuracy at 500 K. Thus a simple closed-form analytical expression for  $Q_r$  could be derived that offers about the same accuracy as a much more complex calculation involving the explicit summation of energy levels that were obtained by diagonalizing the appropriate Hamiltonian matrix.

The present paper treats the rotational partition functions of linear polyatomic molecules. Since analytical expressions are available for the energy levels, this problem may appear trivial compared with the spherical-top case, but

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nevertheless several useful conclusions result. We will develop a quantum correction to the classical partition function that is superior to any existing expression, in that it provides a much better approximation to  $Q_r$  by itself (i.e., without any power-series correction terms), and "converges" more rapidly at very low temperatures when such terms are included. A full treatment of nuclear-spin statistical weights is also provided, which is useful for  $D_{\infty h}$  molecules at extremely low temperatures. Finally, we will consider in detail the magnitudes of the errors introduced by various approximations to  $Q_r$ .

Since the interest here is in linear polyatomic molecules, we will limit our attention to  $^1\Sigma$  electronic states. The results apply, of course, also to  $^1\Sigma$  diatomic molecules. Other authors have considered the calculation of  $Q_r$  for diatomic molecules in arbitrary electronic states.<sup>3-6</sup> Further, we are interested only in the vibrational ground states of these molecules: if degenerate vibrations are excited in a polyatomic molecule, the vibrational angular momentum (or azimuthal) quantum number  $l$  enters into the expression for the rotational energy levels. This contribution, however, is customarily removed and treated as part of the vibrational problem.<sup>4,7-9</sup>

## II. EVALUATION OF $Q_r$ AND THE QUANTUM CORRECTION

For rigid linear molecules in vibrationless  $^1\Sigma$  electronic states, the rotational energy levels are given by

$$E_r = BJ(J+1), \quad (1)$$

where  $J$  is the total angular momentum quantum number and  $B$  is the rotational constant in  $\text{cm}^{-1}$ . Neglecting for the moment nuclear spin, each level has a statistical weight of  $2J+1$ . The rotational partition function is then

$$Q_r = \sum_{J=0}^{\infty} (2J+1)e^{-\beta J(J+1)}, \quad (2)$$

where  $\beta \equiv hcB/kT$ .

The summation of Eq. (2) is given in the literature as either of two equivalent asymptotic expansions,

$$Q_r \sim \beta^{-1} \left[ 1 + \frac{\beta}{3} + \frac{\beta^2}{15} + \frac{4\beta^3}{315} + \cdots \right], \quad (3)$$

$$\sim e^{\beta/4} \beta^{-1} \left[ 1 + \frac{\beta}{12} + \frac{7\beta^2}{480} + \frac{31\beta^3}{8064} + \cdots \right]. \quad (4)$$

Equation (3) is obtained directly by application of the Euler-Maclaurin summation formula to Eq. (2).<sup>4,10</sup> Equation (4) can be derived similarly, after appropriate rearrangement of Eq. (2),<sup>11</sup> but it was first obtained in 1928 by Mulholland,<sup>12</sup> who used less direct techniques of contour integration and the residue theorem.

Equations (3) and (4) are satisfactory at high temperatures (i.e., for small  $\beta$ ), but at lower temperatures their "convergence" is slow. (We use convergence here to indicate an asymptotic approach to the true value; both series ultimately diverge.) In attempting to derive a more satisfactory expression for  $Q_r$ , it is natural to ask whether Eq. (2) can be written in terms of theta functions, for the latter can be converted using the Jacobi transformation into very powerfully convergent series. This approach has been ap-

plied successfully to spherical tops,<sup>2,13</sup> for which  $Q_r$  is given by Eq. (2) except that (again neglecting nuclear spin) the statistical weight is  $(2J+1)^2$  instead of  $2J+1$ . Unfortunately, Eq. (2) itself, although closely related, does not seem to be expressible as a theta function,<sup>11,14,15</sup> and the Jacobi transformation cannot be exploited. Kilpatrick and Kayser<sup>11</sup> have used the similarity of Eq. (2) to a theta-function series to derive a convergent high-temperature expansion for  $Q_r$ . This consists of an asymptotic Euler-Maclaurin expansion which is made convergent by correcting each term with a series of nonanalytic terms in powers of  $\exp(-\pi^2/\beta)$ . However, this formal conversion of an asymptotic into a convergent expansion is of no help in actual computation, for in temperature regimes of practical interest their formula simply reduces to Eq. (4).

Nevertheless, there is an alternative summation of  $Q_r$  that results in a more satisfactory series development than either Eq. (3) or (4). The first two terms of the bracketed correction in Eq. (3) are the start of the power-series representation of  $\exp(\beta/3)$ , which is therefore the most effective first-order correction to  $Q_r \approx \beta^{-1}$ . If this factor is kept, and the series in Eq. (3) is multiplied by the expansion of  $\exp(-\beta/3)$  to compensate, one obtains

$$Q_r \sim e^{\beta/3} \beta^{-1} \left[ 1 + \frac{\beta^2}{90} + \frac{8\beta^3}{2835} + \cdots \right]. \quad (5)$$

The bracketed portion of Eq. (5) is

$$\sum_{n=0}^{\infty} \frac{(-1)^n \beta^n}{12^n n!} \sum_{s=0}^n 3^s (2-4^s) \binom{n}{s} B_{2s},$$

where  $B_{2s}$  denotes the Bernoulli numbers  $B_0 = 1$ ,  $B_2 = 1/6$ ,  $B_4 = -1/30$ ,  $B_6 = 1/42$ ,  $B_8 = -1/30$ , etc. For convenience, the coefficients of terms through  $\beta^8$  in Eq. (5) are given in Table I.

The advantage of Eq. (5) is that the linear correction term is eliminated, and the coefficients of all terms  $\beta^n$  ( $n \geq 2$ ) are smaller than those of either Eq. (3) or (4), so the series can be terminated sooner for a given accuracy. Actually, using just the leading term,  $Q_r \approx \beta^{-1} \exp(\beta/3)$ , provides a quite satisfactory approximation at all except very low temperatures, even without any of the power-series terms in  $\beta$ . This is demonstrated in Table II, which compares the effectiveness in approximating  $Q_r$  of only the first terms of each of the three expansions. Generally three terms of Eq. (3) or (4) are needed to match the accuracy provided by just the first term of Eq. (5).

TABLE I. Coefficients of  $\beta^n$  in Eq. (5).

$n$	Coefficient
0	1
1	0
2	1/90
3	8/2835
4	5/4536
5	148/280 665
6	796 801/2 627 024 400
7	33 533/164 189 025
8	101 458 319/643 095 573 120

TABLE II. Errors in various approximations to  $Q_r$  for linear molecules.

$\beta$	$T$ for HCl/HCN (K)	True $Q_r$	Error, assuming $Q_r$ equals		
			$1/\beta$	$e^{\beta/4}/\beta$	$e^{\beta/3}/\beta$
0.01	1500/213	100.334 001	− 0.33%	− 0.08%	− 0.0001%
0.05	300/43	20.336 699	− 1.7%	− 0.42%	− 0.003%
0.10	150/21	10.340 130	− 3.3%	− 0.84%	− 0.011%
0.20	75/11	5.347 202	− 6.5%	− 1.7%	− 0.047%

The classical rotational partition function for the rigid linear rotator, obtained by integrating instead of summing in Eq. (2), is  $\beta^{-1}$ , i.e., the leading term of Eq. (3). The exponentials in Eqs. (4) and (5) and the series terms in all three equations are corrections that arise from the quantization of the rotational energy levels. Table II demonstrates that the proper first-order quantum correction to  $Q_r \approx \beta^{-1}$  is not  $\exp(\beta/4)$ , as is occasionally stated, but rather  $\exp(\beta/3)$ .

A similar simplifying treatment can be applied to the rotational partition function of symmetric tops, and will be discussed elsewhere.<sup>16</sup>

We remark that it makes no difference which of Eqs. (3), (4), or (5) is used to obtain the derived ideal-gas thermodynamic functions  $-(F^\circ - H^\circ_0)/RT = \ln Q$ ,  $(H^\circ - H^\circ_0)/RT = -\beta d(\ln Q)/d\beta$ , and  $C_p/R = \beta^2 d^2(\ln Q)/d\beta^2$ . Thus, the rotational contribution to the molal enthalpy function is obtained from any of the three expressions for  $Q_r$  as  $[(H^\circ - H^\circ_0)/RT]_r \sim 1 - \beta/3 - \beta^2/45 - \dots$ , etc.

### III. CENTRIFUGAL DISTORTION CORRECTION

Real molecules are, of course, not rigid rotators, and the effect of centrifugal stretching is to replace the rotational energy level formula of Eq. (1) by

$$E_r = BJ(J+1) - DJ^2(J+1)^2 + HJ^3(J+1)^3. \quad (6)$$

It has been well established<sup>4,5,7-10,17-20</sup> that when the energy levels of a linear molecule can be adequately fitted by the first two terms of Eq. (6), the result is to multiply the calculated rigid-rotator partition function by the first-order correction factor

$$f_c = 1 + 2D/B\beta.$$

(Writing  $f_c$  as a multiplying factor is convenient because the correction then appears directly as an additive term to the thermodynamic functions.) Several authors have extended this analysis to cover higher order contributions from the quartic constant  $D$ ,<sup>4,5,17-20</sup> and terms due to the sextic constant  $H$ .<sup>4,17-19</sup> These two effects should be considered together, for terms in  $D^2$  and  $H$  are of the same order. Such treatments have been reported by Giauque and Overstreet,<sup>17</sup> Kassel,<sup>4</sup> and Papoušek<sup>19</sup>; these are essentially equivalent, although they differ in detail because of different choices that were made in keeping or discarding certain very small terms that make only minor contributions to  $Q_r$ .

For this paper, the rotational partition function that results from the energy-level expression of Eq. (6) was rederived in a form appropriate for a quantum correction of  $\exp(\beta/3)$ . The exponentials in  $D$  and  $H$  were expanded in

series form, followed by Euler–Maclaurin summation. All terms and factors were kept throughout the derivation, and decisions on which could be discarded were then made by examining trial calculations on real molecules such as HCN at temperatures up to 5000 K. It could be shown that the following correction factor to the rigid-rotator partition function of Eq. (5) is satisfactory:

$$f_c = 1 + 2d(3 - \beta)/3\beta + 6(2d^2 - h)/\beta^2 + 120d(d^2 - h)/\beta^3, \quad (7)$$

where  $d \equiv D/B$  and  $h \equiv H/B$ . This is of the same form as an analogous expression that gives quite accurate results for spherical-top molecules.<sup>2</sup>

The principal terms of Eq. (7) are equivalent to those that have been derived previously,<sup>4,17,19</sup> but again there are minor differences. Comparisons with exactly summed  $Q_r$  for HCN reveal that the expression of Giauque and Overstreet<sup>17</sup> is somewhat less accurate than the others, for it omits the contribution from  $D^3$  that appears (as  $120d^3/\beta^3$ ) in the last term of Eq. (7). Equation (7) and the formulas of Kassel<sup>4</sup> and Papoušek<sup>19</sup> all give eight- or nine-figure accuracy at temperatures up to 1000 K, and six- or seven-figure accuracy at 5000 K. Interestingly, each of them is better than the others in some temperature region, but these differences are minor and all three provide as much accuracy as is likely to be of practical interest.

Obviously not all terms in Eq. (7) are necessary for every calculation of  $Q_r$ . For many molecules, of course,  $H$  is unknown and must be taken to be zero; and except at quite high temperatures, the contribution of the term in  $(d/\beta)^3$ , and perhaps even that in  $(d/\beta)^2$ , may be negligible.

Woolley<sup>21</sup> has pointed out that for molecular hydrogen a formula like Eq. (6) fails for sufficiently large  $J$ , and is not suitable at temperatures over 2000 K. He derives an alternative inverted series that better describes the higher rotational levels of  $H_2$ , and obtains the resulting rotational partition function. For any molecule other than  $H_2$  at high temperatures, however, Eq. (6) is adequate, and it is universally employed for polyatomic molecules.

### IV. NUCLEAR SPIN STATISTICS

We now consider the influence of nuclear spin on  $Q_r$ . If a linear molecule has a center of symmetry (i.e., belongs to the point group  $D_{\infty h}$ ), then the statistical weight  $2J + 1$  of Eq. (2) must be multiplied by the nuclear spin weights, which are different for levels of even and odd  $J$ . This has an appreciable effect on  $Q_r$  only at very low temperatures: it is well

known<sup>10,12</sup> that the rotational partition functions summed over only even or only odd levels are asymptotically equal to all orders in  $\beta$ , and each equals one-half of the total partition function. Deviations from this equality become significant only for  $\beta > 0.2$ , and hence are of concern chiefly in connection with  $H_2$  (for which  $\beta > 0.2$  at  $T < 427$  K) and its isotopes. Given the potential interest in vapor-phase polyatomic molecules at very low temperatures, however, it may be useful to have a general treatment available, for it is usually quicker to evaluate an analytical expression than to perform a direct summation.

Consider a linear molecule  $W(XYZ\dots)_2$ ; or, equivalently,  $(XYZ\dots)_2$  (for a central atom, if present, will make the same contribution to the statistical weights of all rotational levels, and hence can be neglected for our purposes). For a vibrationless  $\Sigma_g^+$  electronic state, the statistical weight factors follow from the discussion in Herzberg<sup>22</sup>:

$$\begin{aligned} \text{even levels} & \quad \frac{1}{2} I(I + \kappa), \\ \text{odd levels} & \quad \frac{1}{2} I(I - \kappa), \end{aligned} \quad (8)$$

where the nuclear-spin multiplicity for the  $XYZ\dots$  ligand is

$$I = (2I_X + 1)(2I_Y + 1)(2I_Z + 1)\cdots = \prod_i (2I_i + 1), \quad (9)$$

and  $I_X, I_Y, I_Z$  are the spins of the X, Y, Z nuclei. If there is an even number of nuclei following Fermi statistics (i.e., with half-integral spin) in the group of nuclei  $XYZ\dots$ , the resultant statistics of each ligand group is Bose and  $\kappa = +1$  in Eq. (8); if there is an odd number of Fermi nuclei in each group, the resultant statistics is Fermi and  $\kappa = -1$ .

We now construct the partition function as follows, where  $e$  and  $o$  indicate summation over even or odd levels only, and  $t$  indicates summation over all levels:

$$\begin{aligned} Q_r &= \frac{1}{2} I(I + \kappa) \sum_e (2J + 1) e^{-\beta J(J+1)} \\ &+ \frac{1}{2} I(I - \kappa) \sum_o (2J + 1) e^{-\beta J(J+1)} \\ &= \frac{1}{2} I^2 \sum_t (2J + 1) e^{-\beta J(J+1)} + \frac{1}{2} \kappa I Q_{ex}. \end{aligned} \quad (10)$$

The sum in the first term of Eq. (10) is simply the rigid-rotator partition function  $Q_r^0$  of Eq. (5).  $Q_{ex}$  is the exchange partition function<sup>11,15</sup> defined by

$$\begin{aligned} Q_{ex} &\equiv \sum_e (2J + 1) e^{-\beta J(J+1)} - \sum_o (2J + 1) e^{-\beta J(J+1)} \\ &= \sum_t (-1)^J (2J + 1) e^{-\beta J(J+1)}. \end{aligned}$$

$Q_{ex}$  has a null expansion as a power series in  $\beta$ ,<sup>15</sup> a consequence of the asymptotic equivalence of  $Q_e$  and  $Q_o$  mentioned in the opening paragraph of this section. But  $Q_{ex}$  is readily evaluated as a theta function<sup>2,11,15,18</sup>:

$$Q_{ex} = (e^{\beta/4}/2\pi) \theta_1'(0, \beta/\pi) \approx \pi^{3/2} e^{\beta/4} e^{-\pi^2/4\beta} \beta^{-3/2}.$$

We then have

$$\begin{aligned} Q_r &\sim \frac{1}{2} I^2 Q_r^0 + \frac{1}{2} \kappa I \pi^{3/2} e^{\beta/4} e^{-\pi^2/4\beta} \beta^{-3/2} \\ &\sim \frac{1}{2} I^2 e^{\beta/3} \beta^{-1} \left[ 1 + \frac{\beta^2}{90} + \cdots \right. \\ &\quad \left. + \kappa I^{-1} \pi^{3/2} e^{-\beta/12} e^{-\pi^2/4\beta} \beta^{-1/2} \right]. \end{aligned}$$

The factor  $1/2$  appearing here is just  $1/\sigma$ , where  $\sigma$  is the classical symmetry number.

For the hydrogen molecule ( $I_H = 1/2, I = 2, \kappa = -1$ ), an equivalent expression was derived many years ago by Gordon and Barnes.<sup>18</sup>

TABLE III. Rotational partition functions for HCN.

$T$ (K)	$J_{\max}^a$	True $Q_r^b$	Approx. $Q_r^c$	Contribution of			
				$e^{\beta/3}/\beta$	Series <sup>d</sup>	$D^e$	$H^e$
2	2	1.3661	1.3663	1.3404	0.0259	0	0
5	4	2.7152	2.7152	2.7090	0.0062	0	0
10	7	5.0500	5.0500	5.0472	0.0027	0.0001	0
20	10	9.7445	9.7445	9.7429	0.0013	0.0003	0
50	18	23.8474	23.8474	23.8447	0.0005	0.0022	0
100	26	47.3615	47.3615	47.3525	0.0002	0.0087	0
300	44	141.4662	141.4662	141.3877	0.0001	0.0785	0
500	61	235.6417	235.6417	235.4236	0	0.2182	-0.0001
1000	91	471.3876	471.3876	470.5135	0	0.8752	-0.0012
2000	126	944.2047	944.2047	940.6935	0	3.5208	-0.0095
5000	213	2373.4681	2373.4675	2351.2335	0	22.3907	-0.1567

<sup>a</sup> Highest  $J$  value that must be included in the summation to give an accuracy of four decimal places.

<sup>b</sup> Calculated by direct summation, using  $hc/k = 1.438\,786$  cm K and the molecular constants of Knoll *et al.* (Ref. 23):  $B_0 = 1.478\,221\,825$ ,  $D_0 = 2.909\,851 \times 10^{-6}$ ,  $H_0 = 2.72 \times 10^{-12}$  cm<sup>-1</sup>.

<sup>c</sup> Calculated using Eqs. (11) and (7).

<sup>d</sup> Contribution from the terms  $\beta^2/90 + 8\beta^3/2835 + \cdots$  in Eq. (11).

<sup>e</sup> Contributions of quartic ( $D$ ) and sextic ( $H$ ) centrifugal distortion terms. The sum of the four contributing terms (columns 5–8) may differ from the approximate  $Q_r$  (column 4) by one unit in the fourth decimal place due to roundoff.

TABLE IV. Rotational partition functions for C<sub>2</sub>H<sub>2</sub>.

<i>T</i> (K)	<i>J</i> <sub>max</sub> <sup>a</sup>	True <i>Q</i> <sub>r</sub> <sup>b</sup>	Approx. <i>Q</i> <sub>r</sub> <sup>c</sup>	Contribution of			
				<i>e</i> <sup>β/3</sup> /β	Series <sup>d</sup>	<i>I</i> <sup>e</sup>	<i>D</i> <sup>f</sup>
2	3	2.6878	2.6879	3.1330	0.0338	− 0.4789	0
5	5	6.6009	6.6009	6.6126	0.0093	− 0.0210	0
10	9	12.5040	12.5040	12.4996	0.0042	0	0.0002
20	11	24.3065	24.3065	24.3038	0.0020	0	0.0008
50	21	59.7451	59.7451	59.7395	0.0008	0	0.0048
100	29	118.8263	118.8263	118.8066	0.0004	0	0.0192
300	52	355.2551	355.2551	355.0816	0.0001	0	0.1734
500	70	591.8398	591.8398	591.3575	0.0001	0	0.4822
1000	105	1183.9814	1183.9814	1182.0478	0	0	1.9335
2000	148	2371.2013	2371.2013	2363.4287	0	0	7.7726
5000	248	5956.8983	5956.8955	5907.5714	0	0	49.3240

<sup>a</sup>Highest *J* value that must be included in the summation to give an accuracy of four decimal places.

<sup>b</sup>Calculated by direct summation, using *hc/k* = 1.438 786 cm K and the molecular constants of Hietanen and Kauppinen (Ref. 24): *B*<sub>0</sub> = 1.176 640 6, *D*<sub>0</sub> = 1.6221 × 10<sup>−6</sup> cm<sup>−1</sup>.

<sup>c</sup>Calculated using Eqs. (11) and (7).

<sup>d</sup>Contribution of the terms β<sup>2</sup>/90 + 8β<sup>3</sup>/2835 + ⋯ in Eq. (11).

<sup>e</sup>Contribution due to nuclear spin statistics.

<sup>f</sup>Contribution due to the quartic centrifugal distortion term. The sum of the four contributing terms (columns 5–8) may differ from the approximate *Q*<sub>r</sub> (column 4) by one unit in the fourth decimal place due to roundoff.

## V. DISCUSSION

The rotational partition function for linear molecules derived in Secs. II–IV is

$$Q_r \sim \sigma^{-1} I^2 e^{\beta/3} \beta^{-1} \left[ 1 + \frac{\beta^2}{90} + \frac{8\beta^3}{2835} + \cdots + \kappa I^{-1} \pi^{3/2} e^{-\beta/12} e^{-\pi^2/4\beta} \beta^{-1/2} \right] f_c, \quad (11)$$

where  $\beta \equiv hcB/kT$  and the coefficients of further terms in the power series in  $\beta$  are given in Table I. For *D*<sub>∞h</sub> molecules [W(XYZ...)<sub>2</sub> or (XYZ...)<sub>2</sub>], the symmetry number  $\sigma = 2$ , the nuclear-spin multiplicity *I* for the ligand group XYZ... is given by Eq. (9), and  $\kappa = \pm 1$  according to whether the resultant statistics of each ligand group is Bose or Fermi. For *C*<sub>∞v</sub> molecules,  $\sigma = I = 1$  and  $\kappa = 0$ . In both cases the centrifugal distortion correction *f*<sub>c</sub> is given by Eq. (7).

We illustrate the calculation of rotational partition functions of linear molecules with two examples. HCN has *C*<sub>∞v</sub> symmetry, so the nuclear-spin correction to Eq. (11) does not apply ( $\kappa = 0$ ), but both the quartic and sextic centrifugal distortion constants are known.<sup>23</sup> The calculations at temperatures from 2 K to 5000 K are summarized in Table III. The accuracy of Eq. (11) throughout this temperature range is evident.

The last four columns in Table III show the magnitudes of the various contributions to *Q*<sub>r</sub>. As indicated in Table II, the classical partition function with the revised first-order quantum correction,  $Q_r \approx \beta^{-1} \exp(\beta/3)$ , is quite adequate for rigid molecules at temperatures above about 20 K ( $\beta = 0.11$ ); only below this do the power-series terms in Eq. (11) make a contribution of as much as 0.01% to *Q*<sub>r</sub>. When centrifugal distortion is considered, the quartic constant *D* is significant even at moderate temperatures, affecting *Q*<sub>r</sub> by 0.01% at 50 K and by 1% at 5000 K; on the other hand, the sextic term is less than 0.01% of *Q*<sub>r</sub> at 5000 K.

As an example of a *D*<sub>∞h</sub> molecule exhibiting nuclear-spin effects, we consider acetylene, (CH)<sub>2</sub>. Since *I*<sub>C</sub> = 0 and *I*<sub>H</sub> = 1/2, each CH group follows Fermi statistics ( $\kappa = -1$ ) with *I* = 2; the statistical weights used in the direct summation are, from Eq. (8), 1:3 for even:odd *J*. Results are presented in Table IV. The conclusions regarding the influence of the power-series quantum correction terms and of centrifugal distortion are similar to those that apply to HCN. In addition, we see that nuclear spin becomes important only at very low temperatures, below 10 K for C<sub>2</sub>H<sub>2</sub>, but its effect increases rapidly as the temperature is lowered further.

We conclude that Eq. (11) is a satisfactory representation of the rotational partition function of linear molecules in <sup>1</sup>Σ electronic states for a wide temperature range. The effective low-temperature limit is determined by the convergence of Eq. (5); if we accept an error of no more than 0.01% in *Q*<sub>r</sub>, and retain terms through β<sup>8</sup> as given in Table I, this requires that  $\beta < 0.87$ , i.e., *T* > 2.4 K for HCN and 1.9 K for C<sub>2</sub>H<sub>2</sub>, and lower temperatures for most other linear molecules. [The values of *Q*<sub>r</sub> at *T* = 2 K in Tables III and IV were obtained carrying terms through β<sup>9</sup> and β<sup>12</sup>, respectively, in Eq. (11). The number of these terms required drops rapidly with increasing temperature.] At the other extreme, Eq. (11) should provide acceptable accuracy for most molecules to temperatures above 5000 K, provided of course that the centrifugal distortion constants *D* and *H* are known with sufficient precision.

## APPENDIX: OCTIC DISTORTION TERMS

A higher-order treatment of centrifugal distortion results in the addition of an octic term  $-LJ^4(J+1)^4$  to Eq. (6). This in turn changes the final term of Eq. (7) to

$$24(5d^3 - 5dh + l)/\beta^3,$$

where  $l \equiv L/B$ . This result will have no practical effect on

most partition-function calculations, but is given to show how the octic constant enters Eq. (7), which is now complete through terms in  $1/\beta^3$ . It should be noted that  $L$  contributes to the same order as  $D^3$  and  $DH$ .

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