Centrifugal distortions in molecules: An *ab initio* approach

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An *ab initio* approach to the theoretical description of centrifugal distortions in molecules is presented. The method is based on the calculation of the electronic energy changes and gradients accompanying rotationally induced distortions. A centrifugal distortion pathway in nuclear coordinate space is defined. Results are presented at the HF/6-31G** level for NH_3, CH_4, BF_3, and SF_6, and at the Guillemin–Zener level for H_2^+. Quartic centrifugal distortion parameters are computed for each molecule, with distortion anisotropies presented in the form of tensor coefficients. Centrifugally induced electric dipole moment coefficients are presented for CH_4 and BF_3 together with dipole moment changes for NH_3. Agreement with experiment and with conventional theoretical descriptions is generally quite satisfactory, particularly for the tensor coefficients representing the cubic anisotropy in the distortions of the spherical tops CH_4 and SF_6.

I. INTRODUCTION

The distortion of a rotating molecule from its equilibrium geometry has been recognized for a long time by molecular spectroscopists. The effects upon the rovibrational energy levels have usually been expressed in terms of an effective Hamiltonian containing angular momentum operators and empirical coefficients.[1-6] These coefficients, often called centrifugal distortion constants, have proven to be invaluable measures of various aspects of molecular force fields.[7] In fact the traditional theoretical analysis[1-6] of these constants involves their relationship to rotational constants, vibrational frequencies, Coriolis coupling constants, vibrational anharmonicities, etc.

Interest in centrifugal effects has increased in recent years due to the development of high-resolution spectroscopic techniques and to major advances in the theoretical description of highly excited rotational states of molecules. Much of this interest has been focused upon the familiar spherical tops CH_4[4,5,8-18] and SF_6,[18-22] as these molecules display splittings of the $(2J + 1)^2$ degenerate rigid rotator levels. The concept[22,23] of a rotational energy surface portraying the variation of the rotational energy with respect to the direction of the angular momentum in a body-fixed frame has proven to be particularly useful in understanding the clustering patterns of high-J states.

In our present study we present an approach to centrifugal distortions and their associated rotational energy stabilizations which exploits *ab initio* electronic structure computational methods. The approach is direct, bypassing the explicit consideration of related spectroscopic constants as such information is implicitly contained in the *ab initio* electronic energy (nuclear potential energy) hypersurface. Results are presented for H_2^+, NH_3, CH_4, BF_3, and SF_6.

II. METHOD

A. Centrifugal stabilization energies

The basic approach in our study is to use *ab initio* methods to calculate the electronic energy of a molecule distorted from its equilibrium geometry by centrifugal forces. Quasiequilibria are solved for by the requirement that all compo-

nents of the gradient of the sum of the electronic and rotational energies be zero. While our procedure may be applied to any molecule, it is particularly attractive for describing spherical and symmetric tops.

We conveniently describe the atomic positions in a molecule in terms of cylindrical coordinates with the cylinder axis being the chosen (classical) rotational axis passing through the center-of-mass. These coordinates may be used for any principal axis even if it is not a molecular symmetry axis. The set of $3N$ nuclear coordinates $\mathbf{Q}$ is the set $\{d_i, z_i, \phi_i, i = 1, N\}$ where for the ith atom d_i is the distance from the axis, z_i its coordinate parallel to the axis, and ϕ_i is angular position about the axis. The moment of inertia in the z direction is simply

$$I_z = I = \sum_{i=1}^{N} M_i d_i^2, \qquad (1)$$

where M_i is the mass of the ith atom. For special choices of rotation axes for the spherical and symmetric tops considered in this study, only a single value of d_i appears in the expression for I. For example, with a C_3 axis chosen for the rotation of SF_6, I is $6m_F d^2$. Table I gives a list of the cylindrical coordinates used.

We calculate the total electronic energy E_{el} as a function of $\mathbf{Q}$ (see below for details), and specifically minimize $E_{el}(\mathbf{Q})$ with respect to the $2N$ coordinates $\{z_i, \phi_i\}$ for fixed N coordinates $\{d_i\}$. For sufficiently symmetrical cases the gradients of E_{el} with respect to the set $\{\phi_i\}$ of angular coordinates vanish by symmetry, so that in effect these N coordinates are also fixed. The minimization is carried out using *ab initio* analytical gradients; the same gradient algorithms yield values of $\{\partial E_{el}/\partial d_i, i = 1, N\}$ at the constrained minima. Simultaneous solution of the N equations

$$\partial E_{el}/\partial d_i + \partial E_r/\partial d_i = 0, \qquad (2)$$

where E_r is the rotational energy $J(J + 1)/2I$ ($\hbar$ taken as 1 throughout this paper) yields the value of J for which a given distorted structure corresponds to a quasiequilibrium structure. For arbitrary $\{d_i\}$ no solution exists, as the associated structures do not lie on the centrifugal distortion pathway $\mathbf{Q}(J)$. In general the hypersurface must be searched for the

TABLE I. Cylindrical molecular coordinates.

Molecule	Symmetry	Atom	d	z	ϕ
NH_3	C_{3v}	N	0	0	...
		H	d	a	0
		H	d	a	120
		H	d	a	240
	C_s	N	d_1	0	180
		H	d_2	a	0
		H	d_3	$-b$	ϕ
		H	d_3	$-b$	$-\phi$
CH_4	C_{3v}	C	0	0	...
		H	0	a	...
		H	d	$-b$	0
		H	d	$-b$	120
		H	d	$-b$	240
	D_{2d}	C	0	0	...
		H	d	a	0
		H	d	a	180
		H	d	$-a$	90
		H	d	$-a$	270
BF_3	D_{3h}	B	0	0	...
		F	d	0	0
		F	d	0	120
		F	d	0	240
	C_{2v}	B	0	0	...
		F	0	a	...
		F	d	$-b$	0
		F	d	$-b$	180
SF_6	D_{3d}	S	0	0	...
		F	d	a	...
		F	d	a	120
		F	d	a	240
		F	d	$-a$	60
		F	d	$-a$	180
		F	d	$-a$	300
	D_{4h}	S	0	0	...
		F	0	a	...
		F	0	$-a$	...
		F	d	0	0
		F	d	0	90
		F	d	0	180
		F	d	0	270

where $\nabla E_{el}(d)$ is the derivative $\partial E_{el}/\partial d$ at the quasiequilibrium.

Since the gradient of the electronic energy along the centrifugal distortion pathway is nonzero except at the origin (the $J = 0$ equilibrium geometry), the pathway will have contributions only from vibrational modes which are totally symmetric in the point group of the *distorted* molecule. Thus the cylindrical coordinate d for CH_4 with $J||S_4$ (D_{2d} symmetry) has contributions from the T_d modes $\nu_1(a_1)$ and $\nu_2(e)$, while the corresponding d coordinate with $J||C_3$ (C_{3v} symmetry) has contributions from the T_d modes $\nu_1(a_1)$, $\nu_3(t_2)$, and $\nu_4(t_2)$.

We compute a centrifugal stabilization energy ΔE for a given J as the difference between the rigid molecule energy $E_{el}^0 + E_r^0 = E_{el}^0 + J^2/2I_0$, where I_0 is the moment of inertia for the ($J = 0$) equilibrium structure, and the nonrigid molecule energy $E_{el} + E_r = E_{el} + J^2/2I$. Thus

$$\Delta E(J) = J^2(1/2I_0 - 1/2I) - \Delta E_{el}, \qquad (4)$$

where $\Delta E_{el} = E_{el}(J) - E_{el}^0$ is the increase in electronic energy accompanying the displacements $\{d_i\}$ associated with a given J. Finally, a centrifugal distortion constant is obtained by dividing $\Delta E(J)$ by $J^2(J+1)^2$ or, for sufficiently large J, by J^4; the resulting value may or may not be essentially independent of J depending upon the goodness of the quartic description of centrifugal distortion. It should be stressed that our quasistatic model is taken as a description of vibrational ground states only.

B. Electronic structure calculations

The specific method used to obtain the electronic energies and gradients needed in our study is the calculation of all-electron *ab initio* wave functions at the single-determinantal (self-consistent field) level with the GAUSSIAN 80 program.[24] The Gaussian basis set[25-29] 6-31G** with polarization functions for all atoms (p type for H atoms, d type for heavier atoms) was used throughout the study. All six-order Gaussians arising from a d polarization function were employed. This computational level, designated as HF/6-31G**, is generally satisfactory for computing equilibrium geometries and vibrational frequencies, with the latter being typically 10%–15% too large.[30] The calculated bond

solution corresponding to a given J. However, for most of our examples in Table I there is only a single d parameter, so that there is only one equation to solve yielding $J(d)$. For these cases, every $d > d_0$, where d_0 is the ($J = 0$) equilibrium value of d, corresponds to a point on the centrifugal distortion pathway. This pathway is defined by $d(J)$, or more generally the set $\{d_i(J)\}$, together with the set $\{z_i(J), \phi_i(J)\}$ for a given direction of J with respect to the molecular frame. As the corresponding J's are typically large even for displacements of, say, 0.01 Å, we usually neglect the components of J normal to the designated rotation axis and use E_r in the classical form $J^2/2I$. For cases in which I and hence E_r depend on only a single d values, only a single equation of the type in Eq. (2) need be solved, yielding

$$J = [d \cdot I(d) \cdot \nabla E_{el}(d)]^{1/2}, \qquad (3)$$

TABLE II. Equilibrium molecular structures.

Molecule	Symmetry	Parameter[a]	Calc	Obs
H_2^+	$D_{\infty h}$	R	1.058	1.060[b]
NH_3	C_{3v}	R	1.001	1.008[c]
		A	107.6	107.3
CH_4	T_d	R	1.084	1.092[d]
BF_3	D_{3h}	R	1.301	1.307[e]
SF_6	O_h	R	1.544	1.564[f]

[a] R is bond length in Å, A is bond angle in deg.
[b] Reference 33.
[c] Reference 34.
[d] Reference 35.
[e] Reference 36.
[f] Reference 37.

TABLE III. Centrifugal stabilization energies[a] and dipole moment[b] changes.

Molecule	Symmetry	Δd^c	J	ΔE^a	μ^b	$\Delta E/J^4$	$\Delta\mu/J^2$
H_2^+	$D_{\infty h}$	0.030	5	18.6		2.07×10^{-2d}	
		0.082	10	226.2		1.87	
		0.159	15	967.2		1.63	
		0.261	20	2678.2		1.50	
		0.415	25	5589.4		1.32	
NH_3	C_{3v}	0.0064	17.2	12.8	1.794	1.45×10^{-4}	1.46×10^{-4}
		0.0174	28.7	98.1	1.716	1.44	1.47
		0.0374	43.5	484.2	1.561	1.36	1.47
		0.0674	61.0	1711.7	1.284	1.23	1.48
		0.0874	71.6	3035.3	1.058	1.16	1.52
		0.1074	81.6	4815.3	0.769	1.08	1.60
CH_4	C_{3v}	0.02	35.7	131.7	0.030	8.13×10^{-5}	2.36×10^{-5}
		0.04	51.6	550.1	0.060	7.77	2.27
		0.06	64.4	1277.2	0.091	7.41	2.20
		0.08	75.7	2329.2	0.122	7.09	2.13
		0.10	85.9	3698.0	0.153	6.78	2.07
		0.12	95.4	5395.8	0.184	6.51	2.03
		0.14	104.2	7403.6	0.214	6.38	1.97
		0.16	112.5	9697.6	0.244	6.05	1.92
	D_{2d}	0.02	34.0	138.0		1.04×10^{-4}	
		0.04	48.9	561.6		9.80×10^{-5}	
		0.06	62.1	1373.0		9.23	
		0.08	73.6	2547.0		8.70	
		0.10	84.2	4133.0		8.21	
		0.12	94.4	6156.2		7.76	
		0.14	104.1	8632.8		7.34	
		0.16	113.5	11571.0		6.97	
BF_3	D_{3h}	0.005	167.4	18.8		2.40×10^{-8}	
		0.010	236.0	73.5		2.37	
		0.020	332.5	290.7		2.38	
		0.030	405.8	643.8		2.37	
	C_{2v}	0.005	63.5	5.8	0.016	3.58×10^{-7}	3.87×10^{-6}
		0.010	90.2	25.0	0.031	3.78	3.79
		0.020	127.5	99.0	0.068	3.75	4.16
		0.030	157.6	229.0	0.100	3.71	4.01
		0.040	183.6	413.0	0.131	3.63	3.87
		0.050	207.2	656.0	0.160	3.56	3.74
SF_6	D_{3d}	0.010	337.9	80.8		6.20×10^{-9}	
		0.020	478.0	324.1		6.21	
	D_{4h}	0.005	246.2	18.1		4.93×10^{-9}	
		0.010	349.7	73.0		4.88	

[a] Energies in cm^{-1} and defined by Eq (4).
[b] Moments in Debye.
[c] $\Delta d = d - d_0$ in Å; see Table I for definition of d.
[d] For H_2^+, tabulated quantity is $\Delta E/J^2(J+1)^2$.

lengths are typically approximately 1% too small, causing rotational constants to be too large.[31] In the calculation of centrifugal distortion constants, which are proportional to the cube of a rotational constant divided by the square of a vibrational frequency, these two types of errors will tend to cancel, although the imbalance of these errors will lead centrifugal distortion constants which may be as much as 20% too small.

The HF level generally provides a very poor description of dissociation, but as our centrifugal displacements from equilibrium are typically small, its use should be reasonably satisfactory. For H_2^+, for which even a modest J value of, say, 20 corresponds to a large displacement Δd of 0.27 Å, we use the very accurate Guillemin–Zener[32] variational function (see below).

We first compute equilibrium geometries (Table II) using cylindrical coordinates (Table I) and analytical gradient optimization procedures. The structural parameters are

TABLE IV. Vibrational frequencies.[a,b]

Molecule	Symmetry	Mode	Calc	Obs[d]
H_2^+	$D_{\infty h}$	σ_g^+	2350[c]	2321.7[e]
$^{14}NH_3$	C_{3v}	$\nu_1(a_1)$	3704	3337
		$\nu_2(a_1)$	1142	950
		$\nu_3(e)$	3841	3444
		$\nu_4(e)$	1811	1627
$^{12}CH_4$	T_d	$\nu_1(a_1)$	3174	2917
		$\nu_2(e)$	1685	1534
		$\nu_3(t_2)$	3285	3019
		$\nu_4(t_2)$	1469	1306
$^{11}BF_3$	D_{3h}	$\nu_1(a_1')$	943	888[f]
		$\nu_2(a_2'')$	738	691[f]
		$\nu_3(e')$	1575	1452[g]
		$\nu_4(e')$	508	481[g]

[a] In cm^{-1}.
[b] HF/6-31G** level except for H_2^+.
[c] Morse fit to Guillemin–Zener potential energy curve.
[d] Reference 44 except as noted.
[e] Reference 41.
[f] Reference 53 and references contained therein.
[g] Reference 47.

compared in Table II with observed values.[33–37] The d parameter is then incremented in small steps $\Delta d = d - d_0$, with other structural parameters reoptimized. Table III gives the resulting ΔE_{el} values together with the associated J values obtained using Eq. (3); also tabulated are dipole moments as appropriate. These results are analyzed and discussed in Sec. III. In most cases we have computed vibrational frequencies from analytical second derivatives[30] obtained at the HF/6-31G** level with the GAUSSIAN 82 program. These values (Table IV), while not used directly in obtaining our centrifugal distortion constants, are important in assessing the reliability of our results.

C. Hydrogen molecular ion

For H_2^+ a somewhat different approach was used. Instead of a Gaussian expansion, we used the very accurate two-parameter Guillemin–Zener (GZ) function[32]

$$\psi_{GZ}(\lambda,\mu) = Ne^{-\alpha\lambda}\cosh(\beta\mu), \tag{5}$$

where N is the normalization constant, λ and μ are the elliptical coordinates defined in terms of the internuclear distance R and the distances r_a and r_b by

$$\lambda = (r_a + r_b)/R, \tag{6a}$$

$$\mu = (r_a - r_b)/R, \tag{6b}$$

and α and β are the variational parameters. Patel[38] has shown that the familiar two-parameter James function[39] is an approximation to ψ_{GZ}; the latter has the correct asymptotic behavior for large R while the James function does not. The even more familiar single-ξ LCAO function corresponds to the special case of ψ_{GZ} with $\alpha = \beta = \xi R/2$.

Instead of specifying an internuclear separation R and then solving for the J values for which

$E(R,J) = E_{el}(R) + E_r(R,J)$ is a minimum, we were able for H_2^+ to invert the procedure, specifying J and solving for the distance R. As the J values were typically much smaller than those considered for the larger molecules, we kept E_r in the form $J(J + 1)/2I$. The parameters α and β were taken as the values minimizing E_{el} for each R; the minimum for $J = 0$ is at $R = 1.999$ bohr $= 1.058$ Å, for which $\alpha = 1.353$, $\beta = 0.918$, and $E_{el} = -0.602\,443$ a.u.

III. RESULTS AND DISCUSSION

A. H_2^+

The simplest molecule studied is H_2^+, described by the Guillemin–Zener (GZ) function[32] in Eq. (5). The centrifugal distortion for a given J is large (Table III), with the ratio $\Delta E/J^2(J + 1)^2$ being approximately 2.0×10^{-2} cm^{-1}, although decreasing in an approximately linear manner for increasing J. Our value is nearly identical to that obtained using conventional theory[40] and empirical parameters,[33,41] namely

$$D = 4B_e^3/\omega_e^2, \tag{7}$$

where B_e and ω_e are the rotational constant and vibrational frequency at equilibrium; using $B_e = 30.21$ cm^{-1} and $\omega_e = 2321.7$ cm^{-1}, $D = 2.04\times10^{-2}$ cm^{-1}. The GZ potential energy curve yields values of $B_e = 30.00$ cm^{-1} and $\omega_e = 2350$ cm^{-1} (Morse fit), which used in Eq. (7) gives $D = 1.96\times10^{-2}$ cm^{-1}.

Of additional interest is the value of R for which the sum of electronic and rotational energies is a maximum, corresponding to a barrier to dissociation. Figure 1 shows both this R_{max} as well as R_{min} (the position of the quasiequilibrium) vs J. The values converge to an R of 5.25 bohr or 2.72 Å for $J = 43$ (nearest integer); at this R the total energy is
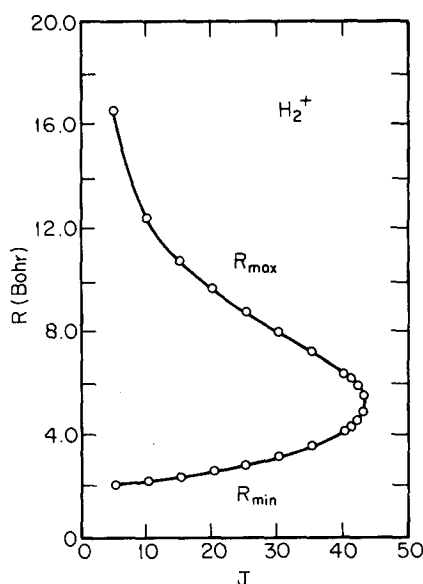

FIG. 1. Internuclear distances in bohr vs J for the minimum (R_{min}) and maximum (R_{max}) of the effective potential energy (electronic plus rotational) for H_2^+ as described by the Guillemin–Zener wave function in Eq. (5).

— 0.482 94 a.u. or 3745 cm^{-1} *above* the dissociation limit. These R values are simply stationary points on the effective potential energy curve as illustrated by Herzberg[42] for HgH. To obtain the energy of the $v = 0$ state for a given J, we must add the J-dependent zero-point energy (ZPE). We have estimated the change in the ZPE from the second derivative of the effective potential energy to be approximately $- 1.5$ $J(J + 1)$ cm^{-1}; the contribution to $\Delta E / J^2 (J + 1)^2$ is only 2×10^{-3} cm^{-1} for $J = 25$ and thus does not significantly change the centrifugal distortion constant.

B. NH$_3$

Centrifugal distortion effects accompanying the rotation of NH$_3$ about the C_3 axis are moderately large due to the softness of the "inversion" mode. The symmetric top energy levels are given in our classical description by

$$E(J_x, J_y, J_z) = AJ_z^2 + B(J_x^2 + J_y^2) , \qquad (8)$$

where A and B are in general implicit functions of $\mathbf{J}$. Letting A_0 and B_0 be the equilibrium values of these constants and neglecting all nonclassical terms as well as terms higher than J^4, the rotational energy may be written

$$E(J_x, J_y, J_z) = A_0 J_z^2 + B_0 (J_x^2 + J_y^2)$$
$$- (D_J + D_{JK} + D_K) J_z^4 - (2D_J + D_{JK})$$
$$(J_x^2 J_z^2 + J_y^2 J_z^2) - D_J [(J_x^4 + J_y^4) + 2J_x^2 J_y^2] \qquad (9)$$

which for $\mathbf{J} \| C_3$ (the z axis) reduces to

$$E(0,0,J_z) = A_0 J_z^2 - (D_J + D_{JK} + D_K) J_z^4 . \qquad (10)$$

The selection of $\mathbf{J} \| C_3$ thus corresponds to a classical description of the quantum states $|J,K \rangle = |J, \pm J \rangle$. Thus our computed contrifugal stabilization energies $\Delta E / J^4$ for $\mathbf{J} \| C_3$ (Table III) are associated with the last term in Eq. (10), namely

$$\Delta E / J^4 = D_J + D_{JK} + D_K . \qquad (11)$$

Our $\Delta E / J^4$ value of 1.67×10^{-4} cm^{-1} obtained by an extrapolation (Fig. 2) of the results in Table III is comparable to an experimental value[43] of $(1.8410 \pm 0.0011) \times 10^{-4}$
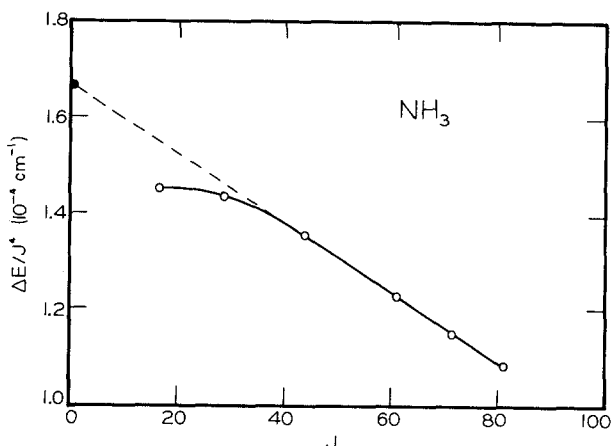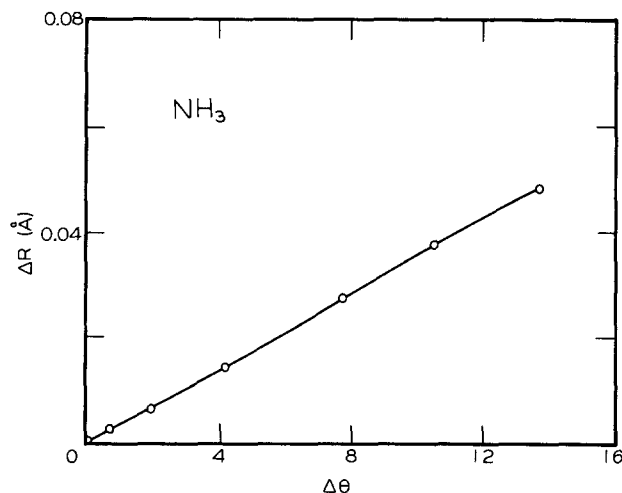
FIG. 3. Centrifugal distortion pathway as change ΔR in Å in bond length vs change $\Delta \theta$ in polar angle in degrees for NH$_3$ at the HF/6-31G** level with $\mathbf{J} \| C_3$. Equilibrium values (Table II) are $R = 1.001$ Å and α (bond angle) $= 107.6°$, corresponding to $\theta = 68.7°$. The J values are 0 at the origin and the six values from Table III at the other points.

cm^{-1} for $D_J + D_{JK} + D_K$ obtained by combining values of D_J, D_{JK}, and D_K. Each D is taken as the mean of the values for the symmetric and antisymmetric inversion states. Specifically, D_J D_{JK}, and D_K are taken as 8.4107, $- 15.5492$, and 8.9795 (each in 10^{-4} cm^{-1}), respectively, so that there is considerable cancellation in their sum. Our value for the sum of these constants is approximately 9% lower than the observed value, reflecting the fact that the HF/6-31G** potential energy hypersurface has excessive curvature near the equilibrium geometry. This is seen most clearly in a comparison (Table IV) of calculated and observed[44] vibrational frequencies, the former being typically 12% too large as expected.[30]

The remaining important feature of the centrifugal distortion of NH$_3$ with $\mathbf{J} \| C_3$ (C_{3v} constraint) are the pathway and the change in the dipole moment. The pathway is shown in Fig. 3 in the form of the change in the bond length R vs the change in the polar angle $\theta = \cot^{-1}(a/d)$ [see Table I: the bond angle α is related to θ by $(3/2)\sin^2 \theta = (1 - \cos \alpha)$]. The equilibrium values at the HF/6-31G** level are $R = 1.001$ Å and $\theta = 68.7°$.

Table III lists the dipole moments vs J; there is a drop of nearly 1 D at $J = 82$, as compared to $J = 0$. The change $\Delta \mu$ is essentially quadratic, with $\Delta \mu / J^2 = - 1.5 \times 10^{-4}$ D (Tables III and IV). Our computed moment for $J = 0$ (without vibrational averaging), namely 1.79 D, is larger than the observed[45] vibrational ground-state value of 1.468 D, so that our computed changes $\Delta \mu$ are probably also too large.

In addition to having considered $\mathbf{J} \| C_3$, we have also considered $\mathbf{J} \perp C_3$, for which the molecular symmetry is C_s if $\mathbf{J}$ lies in a plane containing the original C_3 axis and a N–H bond direction. Thus for $\mathbf{J} \| x$, Eq. (9) reduces to

$$E(J_x, 0, 0) = B_0 J_x^2 - D_J J_x^4 , \qquad (12)$$

a classical description corresponding to the states $|J,K \rangle = |J,0 \rangle$. Although the electronic energy is a function of only four independent internal coordinates, we found it

FIG. 2. Centrifugal stabilizations $\Delta E / J^4$ in cm^{-1} vs J for NH$_3$ at the HF/6-31G** level with $\mathbf{J} \| C_3$. Data are from Table III with ΔE defined by Eq. (4).

TABLE V. Centrifugal distortion parameters[a]

Molecules	Parameter	Calc	Literature
H_2^+	D	2.0×10^{-2}	2.01×10^{-2} [b]
$^{14}NH_3$	D_J	6.6×10^{-4}	$(8.4107 \pm 0.004) \times 10^{-4}$ [c]
	$D_{JK} + D_K$	-4.9×10^{-4}	$(-6.5697 \pm 0.0020) \times 10^{-4}$ [c]
	θ_z^{zz}	-1.5×10^{-4}	...
$^{12}CH_4$	D_s	1.02×10^{-4}	$(1.1087\,76 \pm 0.000\,74) \times 10^{-4}$ [d]
	D_t	4.5×10^{-6}	$(4.434\,515 \pm 0.000\,123) \times 10^{-6}$ [e]
	θ_x^{yz}	4.2×10^{-5}	2.6×10^{-5} [f]
$^{11}BF_3$	D_J	3.8×10^{-7}	$(4.38 \pm 0.10) \times 10^{-7}$ [g]
	D_{JK}	-6.7×10^{-7}	$(-9.1 \pm 1.0) \times 10^{-7}$ [g]
	θ_x^{xx}	4.0×10^{-6}	1.26×10^{-6} [h]
$^{32}SF_6$	D_s	5.68×10^{-9}	$(5.547\,43 \pm 0.000\,43) \times 10^{-9}$ [i]
	D_t	-2.0×10^{-10}	$-(1.8994 \pm 0.0064) \times 10^{-10}$ [i]

[a] Values in cm^{-1} except θ values in Debye.
[b] Derived using Eq. (7) and parameters from Ref. 33.
[c] Reference 43.
[d] Reference 15.
[e] Reference 14.
[f] Reference 9.
[g] Reference 50.
[h] Reference 56.
[i] Reference 60.

more convenient to employ the set of of six cylindrical coordinate variables given in Table I. The rotational energy depends on the three d_i's, so that the quasiequilibria correspond to solutions of a set of six equations, three of the type in Eq. (2) and three of the conventional type for an extremum, namely $(\partial E_{el}/\partial Q_i) = 0$. By using linear interpolations of electronic gradients calculated at closely spaced points (spacings of 0.003 to 0.01 Å) near a solution, we have located three solutions corresponding to J's from 9 to 24. Identifying the associated centrifugal stabilization energies with the term $D_J J_x^4$ in Eq. (12) leads to a value of $D_J = 6.6 \times 10^{-4}$ cm^{-1} for this $K = 0$ case. This calculated value is somewhat smaller (Table V) than the experimental value[43] of $(8.4107 \pm 0.0004) \times 10^{-4}$, probably for the same reasons as described above.

To obtain a value of the third tensor coefficient D_{JK} we should consider $\mathbf{J}$ to be inclined at an angle other than 90° from the $C_3(z)$ axis. However, such rotations, for which the angular velocity ω is not parallel to $\mathbf{J}$, are not dynamically balanced even for a rigid body and are thus not amenable to our static treatment. We do compare in Table V our value of -4.9×10^{-4} cm^{-1} for the combination $D_{JK} + D_K$, obtained from our values of D_J and $D_J + D_{JK} + D_K$, with a literature value of $(-6.5697 \pm 0.0020) \times 10^{-4}$ cm^{-1}; again, as expected, the calculation value is somewhat smaller in magnitude than the observed.

C. CH_4

Our treatment of CH_4 is similar to that of NH_3; specifically we have considered not only $\mathbf{J}||C_3$ but also $\mathbf{J}||S_4$, thus

obtaining the tetrahedral anisotropy in the centrifugal stabilization as described below. We designate the S_4 axes as the Cartesian axes x, y, and z. Thus for $\mathbf{J}||C_3$, $J_x = J_y = J_z = |\mathbf{J}|/\sqrt{3}$, while for $\mathbf{J}||S_4$, $J_x = J_y = 0$, $J_z = |\mathbf{J}|$. Again, we make the high-J classical approximation that $|\mathbf{J}| = J$ rather than $[J(J+1)]^{1/2}$.

The calculations for $\mathbf{J}||C_3$ (C_{3v} symmetry) closely parallel those for NH_3 except that the optimizations for fixed d include optimization with respect to the axial C–H bond length (Table I). Figure 4 shows the centrifugal distortion pathway in the form of the changes in R_{ax} (ax = axial) and R_{eq} (eq = equatorial) vs the change in the polar angle $\theta = \cot^{-1}(b/d)$ (see Table I). The changes in R_{ax} are slight, while those in R_{eq} are as expected appreciable. The corresponding pathway for $\mathbf{J}||S_4$ (D_{2d}) symmetry is shown in Fig. 5.

The quartic centrifugal terms may be written, following Hecht's notation,[4] as

$$E_4 = -D_s J^2(J+1)^2 - D_t O_{pppp}, \tag{13}$$

where O_{pppp} is the tensor operator

$$O_{pppp} = 4(J_x^4 + J_y^4 + J_z^4) - 6(J_x^2 J_y^2 + J_y^2 J_x^2 + J_x^2 J_z^2 + J_z^2 J_x^2 + J_y^2 J_z^2 + J_z^2 J_y^2) + 2(\mathbf{J})^2. \tag{14}$$

Again approximating $J^2(J+1)^2$ by J^4 and dropping the term in $(\mathbf{J})^2$,

$$E_4(C_{3v}) = -D_s J^4 + 24 D_t J^4/9, \tag{15a}$$

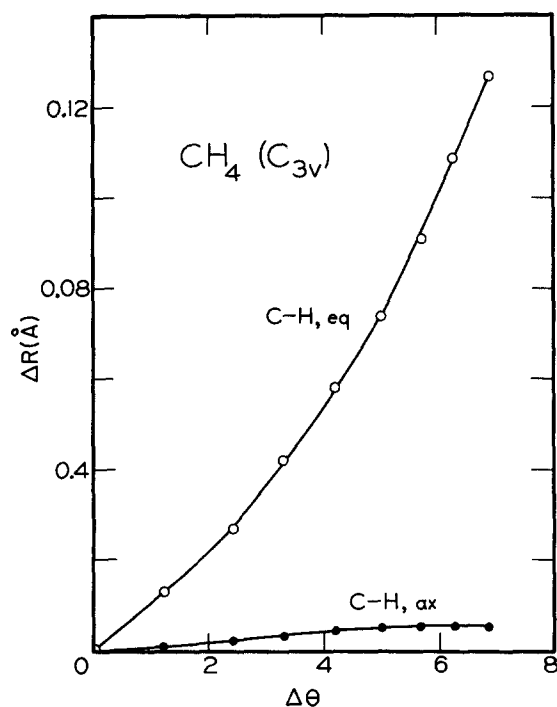$$E_4(D_{2d}) = -D_s J^4 - 4 D_t J^4. \tag{15b}$$

FIG. 4. Centrifugal distortion pathways as changes ΔR in Å in equatorial (eq) and axial (ax) bond lengths vs change $\Delta\theta$ in polar angle in degrees for CH_4 at the HF/6-31G** level with $J||C_3$ (C_{3v} symmetry). The J values are 0 at the origin and the eight values from Table III at the other points. Equilibrium value (Table II) of R_{eq} and R_{ax} is 1.084 Å.

Thus

$$D_s = [2\Delta E(D_{2d}) + 3\Delta E(C_{3v})]/5J^4, \tag{16a}$$

$$D_t = 3[\Delta E(D_{2d}) - \Delta E(C_{3v})]/20J^4, \tag{16b}$$

where $\Delta E(D_{2d})$ and $\Delta E(C_{3v})$ are the centrifugal stabilization energies for a given J of the deformed structures with $J||S_4$ and $J||C_3$, respectively (Fig. 6). Extrapolating $\Delta E(D_{2d})/J^4$ and $\Delta E(C_{3v})/J^4$ from Table III as 1.2×10^{-4} and 0.9×10^{-4} cm^{-1}, respectively, we obtain $D_s = 1.0\times10^{-4}$ cm^{-1} and $D_t = 4.5\times10^{-6}$ cm^{-1}. These values compare very favorably both with experimental val-
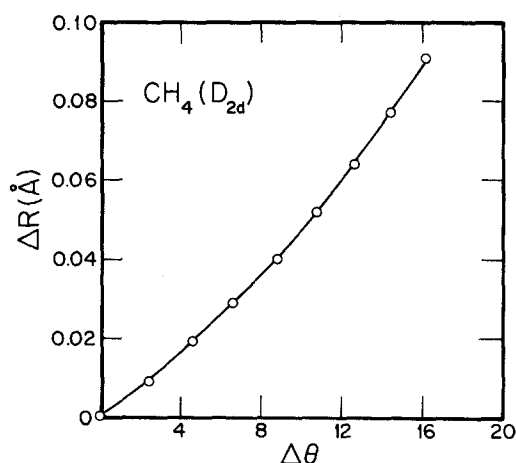
FIG. 5. Centrifugal distortion pathway for CH_4 similar to that in Fig. 4 but for $J||S_4$ (D_{2d} symmetry).
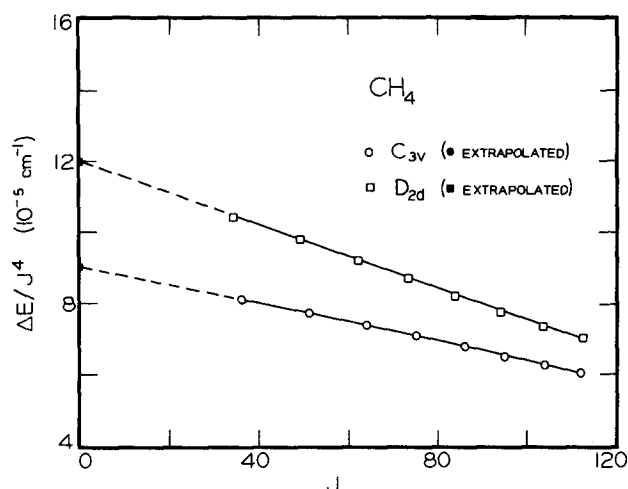
FIG. 6. Centrifugal stabilizations $\Delta E/J^4$ in cm^{-1} vs J for CH_4 at the HF/6-31G** level with $J||C_3$, (O, C_{3v} symmetry) and with $J||S_4$, ($\square$, D_{2d} symmetry). Data are from Table III with ΔE defined by Eq. (4).

ues,[14,15] $D_s = (1.108\ 64 \pm 0.000\ 74)\times10^{-4}$ cm^{-1} and $D_t = 4.434\ 515\times10^{-6}$ cm^{-1}, and with conventional theoretical estimates[4] $D_s = 1.0\times10^{-4}$ cm^{-1} and $D_t = 4.0\times10^{-6}$ cm^{-1}; the latter values are derived from other experimental constants.

The positive sign of D_t for CH_4 corresponds to $E(D_{2d}) < E(C_{3v})$ for a given J. In Table III we list the induced dipole moment in debye divided by J^2 vs J for $J||C_3$. The induced moment has been shown[9] to have Cartesian components

$$\mu_x = \theta_x^{yz}J_yJ_z, \tag{17a}$$

$$\mu_y = \theta_y^{xz}J_xJ_z, \tag{17b}$$

$$\mu_z = \theta_z^{xy}J_xJ_y, \tag{17c}$$

where the coefficient $\theta_x^{yz} = \theta_y^{xz} = \theta_z^{xy} = \theta$. Thus μ is zero for $J||S_4$ since $J_x = J_y = 0$; for $J||C_3$, $\mu_x = \mu_y = \mu_z = \theta J^2/3$ since $J_x = J_y = J_z = J/\sqrt{3}$, so that we obtain θ from

$$\theta = 3^{1/2}|\mu(J)|/J^2. \tag{18}$$

(Note that as before $|J|$ is taken in units of $\hbar$ as J rather than $[J(J+1)]^{1/2}$.) From Table II we see that μ/J^2 is roughly constant, yielding a θ value (Table V) of approximately 4.2×10^{-5} D. This value is comparable to but somewhat larger than the value of 2.6×10^{-5} estimated[9] from a conventional analysis.

We have used the example of CH_4 with $J||S_4$ (D_{2d}) to test the assumption stated in Sec. III A for H_2^+ that the contribution to the centrifugal stabilization energy from the change in the zero-point energy (ZPE) is negligible. Specifically we have used the GAUSSIAN 82 program to calculate vibrational frequencies from analytical second derivatives[30] of the HF/6-31G** energy at the various points on the centrifugal distortion pathway. The resulting frequencies, which as expected[30] are on the average 9.8% too large at the ($J = 0$) equilibrium geometry, correspond to a ZPE whose change with J for $J||S_4$ is found to be approximately $-0.115\ J^2$ cm^{-1} (the negative sign corresponds to a decrease). This is the electronic contribution to ΔZPE, with an

expected actual value of approximately $-0.10 J^2$ cm^{-1}. In addition there is a rotational contribution from E_r. From values of $(\partial^2 E_r/\partial d^2)$ at the quasiequilibria along the pathway $d(J)$ we have calculated the rotational contribution to ΔZPE to be approximately $+0.03 J^2$ cm^{-1}. This change is associated with the two modes of a_1 symmetry for the D_{2d} molecule. Thus the net ΔZPE is approximately $-0.07 J^2$ cm^{-1}, making a positive but small contribution to the centrifugal distortion constant for large J (approximately an 11% increase for $J = 84$).

D. BF₃

The planar symmetric top is readily treated by our procedure, both for $J||C_3$ (D_{3h} symmetry) and for $J||C_2$ (C_{2v} symmetry). As the first of these cases involves only the totally symmetric stretching mode, the stabilizations are very small. Since the constants D_J, D_{JK}, and D_K in Eq. (9) are related[46] by $D_{JK} = -2(D_J + 2D_K)/3$ for a planar symmetric top, while $B_0 = 2A_0$, Eq. (10) reduces to

$$E(0,0,J_z) = A_0 J_z^2 - D_0 J_z^4 , \qquad (19)$$

where

$$D_0 = D_J + D_{JK} + D_K = (D_J - D_K)/3 . \qquad (20)$$

Thus for sufficiently high J, $\Delta E/J^4$ for $J||C_3$ corresponds to D_0; from Table III this coefficient is approximately 2.37×10^{-8} cm^{-1}. Associating the case $J||C_2$ (C_{2v} symmetry) with $E(J_x,0,0)$, for which

$$E(J_x,0,0) = B_0 J_x^2 - D_J J_x^4 , \qquad (21)$$

the stabilization $\Delta E/J^4$ of approximately 3.8×10^{-7} cm^{-1} corresponds to D_J. Combining this value with that of D_0 yields $D_K = 3.1 \times 10^{-7}$ and $D_{JK} = -6.7 \times 10^{-7}$ cm^{-1}. A number of experimental determinations or estimations of these constants have been reported,[36,47–52] with one of the more reliable [50] being that from the pure rotational Raman spectrum of ^{11}BF₃. The reported constants $D_J = (4.38 \pm 0.10) \times 10^{-7}$ and $D_{JK} = (-9.1 \pm 1.0) \times 10^{-7}$, are, as with the NH₃ values, larger in magnitude than our calculated values, again reflecting our vibrational frequency errors (Table IV). The centrifugal distortion for $J||C_3$ involves only the a_1 mode (6% error), while the distortion for $J \perp C_3$ involves in addition one component of each of the e' modes (8% and 6% errors, respectively), where the errors refer to the differences between HF/6-31G* and observed[36,53–55] frequencies.

The induced dipole moment for BF₃ is described[9] by the single coefficient $\theta_x^{xx} = -\theta_x^{yy} = -\theta_y^{xy} = \theta$, with x the C_2 axis, such that

$$\mu_x = \theta [J_x^2 - J_y^2] , \qquad (22a)$$

$$\mu_y = -\theta J_x J_y , \qquad (22b)$$

$$\mu_z = 0 . \qquad (22c)$$

From the values in Table III of μ_x/J_x^2 vs J for $J||C_2$ the coefficient θ is found to be approximately 4.0×10^{-6} D (Table V), somewhat larger than an earlier estimate[56] of 1.26×10^{-6} D. The possibility of observing the pure rotational spectrum of BF₃ has been discussed[57] in terms of this moment.

E. SF₆

The largest molecule we have considered is perhaps the most important in terms of the interest[18–22,58–60] in its rotational energy levels. The expressions (15) and (16) apply directly to SF₆ if the labels C_{3v} for $J||C_3$ and D_{2d} for $J||S_4$ are replaced by D_{3d} for $J||C_3$ and D_{4h} for $J||C_4$. From the results in Table III we obtain $\Delta E/J^4$ values of approximately 6.2×10^{-9} and 4.9×10^{-9} cm^{-1} for D_{3d} and D_{4h} symmetries, respectively. Using Eq. (16), we obtain $D_s = 5.68 \times 10^{-9}$ cm^{-1} and $D_t = -2.0 \times 10^{-10}$ cm^{-1}. The latter coefficient, to which the cubic splittings of the spherical top levels are related, is essentially equal to the observed[19,59] values of $-(1.9 \pm 0.2) \times 10^{-10}$ and $-(1.814 \pm 0.013) \times 10^{-10}$ cm^{-1}. The negative sign corresponds to $E(D_{3d}) < E(D_{4h})$ for a given J. Our calculated value of D_s, however, is significantly smaller than a value of $(1.6 \pm 0.8) \times 10^{-8}$ cm^{-1} obtained from Raman spectra,[58] yet much larger than a value of $(6.2 \pm 1.1) \times 10^{-10}$ cm^{-1} obtained from Doppler-free two-photon spectra.[59] As our values of both D_s and D_t for CH₄ are in essential agreement with experiment (Table V), we have a modest level of confidence in our procedure. We do note the recent preliminary report[60] of a value for D_s of $(5.547\,43 \pm 0.000\,43) \times 10^{-19}$ cm^{-1} based on an analysis of the ν_3 fundamental and in good agreement with our computed value of 5.68×10^{-9} cm^{-1}; also reported was an improved value for D_t, namely $-(1.8994 \pm 0.0064) \times 10^{-10}$ cm^{-1}.

The energy preference for a given J, namely D_{3d} over D_{4h}, is easily understood in terms of the vibrational modes contributing to the centrifugal distortion pathway. Aside from the totally symmetric (ν_1, stretching) contribution, the D_{3d} and D_{4h} pathways contain t_{2g} (ν_5, bending) and e_g (ν_2, stretching) contributions, respectively. The lower-frequency ν_5 mode contribute more to the D_{3d} pathway than the higher-frequency ν_2 mode does to the D_{4h} pathway, leading to greater centrifugal stabilization for the former. Specifically we find for the D_{4h} case with $J = 246$ an increase in the equatorial bond lengths of 0.005 Å accompanied by a slight decrease of 0.001 Å in the axial bond lengths, while for the D_{3d} case with $J = 338$ an increase of 0.005 Å in all bond lengths is accompanied by an increase of 0.4° in the polar angular coordinate of each atom. The latter angular displacement corresponds to a 0.011 Å displacement along a circular arc with radius of 1.554 Å, the computed equilibrium S–F distance.

IV. SUMMARY

In this study we have presented an *ab initio* approach to the theoretical description of centrifugal distortions in molecules. The method is based on the calculation of the electronic energy changes and gradients accompanying rotationally induced distortions. A limitation arises from the fact that our geometry optimizations are typically numerically valid to approximately ± 0.001 Å or 0.1°, corresponding to residual forces of approximately $\pm 4 \times 10^{-4}$ a.u. Thus we cannot describe the very small centrifugal distortions associated with low J values. The variation of the centrifugal stabilization energy along a distortion pathway in nuclear coordinate space may be fitted to a traditional effective Ha-

miltonian, permitting the extraction of centrifugal distortion energy parameters. Centrifugally induced dipole moment changes are similarly computed. Agreement with experiment and with conventional theoretical descriptions is generally quite satisfactory for the molecules considered (Table V). Particularly pleasing is the agreement with experiment for the tensor coefficients representing the cubic anisotropy in the distortions of the spherical tops CH_4 and SF_6. This agreement gives us a moderate level of confidence in the ability of the method to provide semiquantitatively correct values of such difficult to measure parameters as the scalar centrifugal distortion constant for SF_6.

ACKNOWLEDGMENTS

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