

Centrifugal Distortions in Linear Triatomic Molecules: Application of an ab Initio Approach to HCP

LAWRENCE L. LOHR

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109-1055

Our previously outlined method (*J. Mol. Struct. THEOCHEM* **99**, 265–270, 1989) for employing analytic quantum chemical gradients to calculate the geometries, energies, and quartic spectroscopic constants for centrifugally distorted molecules is extended to describe noncentrosymmetric linear triatomic molecules. Results obtained at the HF/6-31G** and CISD/6-31G** levels are presented for the molecule H¹²CP and its isotopic variants D¹²CP, H¹³CP, and D¹³CP.

© 1993 Academic Press, Inc.

INTRODUCTION

The distortion of a rotating molecule from its equilibrium geometry and its effect upon energy levels has been recognized for a long time by molecular spectroscopists. Interest in these centrifugal effects, as they are often called, 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. In a series of studies (1–6) we presented a new approach to centrifugal distortions and their associated rotational energy stabilizations which exploits ab initio electronic structure computational methods. This approach is direct, bypassing in the simplest applications the explicit calculation of spectroscopic constants such as vibrational frequencies as this information is implicitly contained in the ab initio electronic energy hypersurfaces. Specifically, the method is particularly useful at any computational level for which analytic gradients of potential-energy hypersurfaces are available. Results were presented in our first study (1) for H₂⁺, NH₃, CH₄, BF₃, and SF₆. More detailed studies followed of H₂O (2), O₃ (3), and PH₃ (4), as well as an outline of a generalized extension of the method (5). The procedure is structurally oriented, that is, it focuses on the question of the size and shape of molecules with nonzero rotational angular momentum. Centrifugal distortion spectroscopic constants are a very useful form of our computational output, providing an important and indispensable basis for comparison to experimental observations, yet their computation is in a way secondary to the main task. Stated differently, our studies are an exploration of molecular energy in those regions of the nuclear-coordinate hyperspace which are accessible by centrifugal distortions from the equilibrium geometry. In the most recent (6) of our studies we obtained closed-form analytic expressions parametric in the centrifugal displacement for the classical rotational energy of a harmonic oscillator, Morse oscillator, and Lennard–Jones 6-12 oscillator. These expressions were used to construct Padé approximants for the rotational energy dispersion.

In the present study we explore the application of our methods to the rotational energy of noncentrosymmetric triatomic molecules. The corresponding centrosymmetric triatomic case needs no elaboration, as its description is formally the same as that of a homonuclear diatomic molecule. However, the noncentrosymmetric triatomic

involves simultaneous solution of two equations (see below) to obtain the quasi-equilibrium structures which lie along the centrifugal distortion pathway. We illustrate the general procedure with calculations for the methinophosphide (HCP) molecule; this molecule has been the subject of many spectroscopic investigations (7–20) including our combined experimental and ab initio determinations (18) of the bending potential. In that study an ab initio potential was found to be in excellent agreement with a rigid bender model fitted to energy levels going up to $17\,500\text{ cm}^{-1}$ in a single bending mode, and comparisons were made to the analogous HCN/HNC system (21). The molecule HCP has been the subject of a number of other computational investigations (22–25), with several of these (22, 23) focusing upon the calculation of spectroscopic constants. Specifically, results have been reported (22) based on use of the coupled electron pair approximation (CEPA) within the self-consistent electron pair formalism (SCEP). Empirical corrections were introduced both for the reference geometry and for the quadratic potential energy function terms, the latter to yield a fit to the observed wavenumbers for the most abundant isotopic species. By contract our results are not empirically corrected, but consequently are not in as good agreement with experiment.

METHOD

We illustrate here the application of our method to a linear triatomic molecule ABC, for which the moment of inertia depends upon two structural variables. We define a reduced mass matrix \mathbf{M} by

$$\mathbf{M} = (1/M) \begin{pmatrix} m_a(m_b + m_c) & m_a m_c \\ m_a m_c & m_c(m_a + m_b) \end{pmatrix} \quad (1)$$

where m_a , m_b , and m_c , are the masses of A, B, and C, respectively, and M is the molecular mass $m_a + m_b + m_c$. The moment of inertia I may then be written as

$$I = \tilde{\mathbf{R}}\mathbf{M}\mathbf{R}, \quad (2)$$

where \mathbf{R} is the column vector with components R_{ab} and R_{bc} , and $\tilde{\mathbf{R}}$ is the (row) transpose of \mathbf{R} . The gradient ∇E_r of the rotational energy $E_r = \hbar^2 J(J+1)/2I$ may then be written as

$$\nabla E_r = -(2E_r/I)\mathbf{M}\mathbf{R}. \quad (3)$$

The condition for quasi-equilibrium is that $\nabla(E_r + E_{el}) = 0$, where E_{el} is the total electronic energy. Thus

$$\nabla E_{el} = (2E_r/I)\mathbf{M}\mathbf{R}, \quad (4)$$

giving a ratio

$$\frac{(\partial E_{el}/\partial R_{ab})}{(\partial E_{el}/\partial R_{bc})} = \frac{(M_{11}R_{ab} + M_{12}R_{bc})}{(M_{12}R_{ab} + M_{22}R_{bc})}, \quad (5)$$

where M_{ij} is element ij of \mathbf{M} . For $\text{H}^{12}\text{C}^{31}\text{P}$ this ratio becomes

$$\frac{(\partial E_{el}/\partial R_{CH})}{(\partial E_{el}/\partial R_{CP})} = \frac{(1.3874R_{CH} + R_{CP})}{(R_{CH} + 12.9068R_{CP})}, \quad (6)$$

where both the numerator and the denominator of the right-hand side of Eq. (5) have been divided by $m_a m_c = m_{\text{H}} m_{\text{P}}$.

The computational procedure for finding structures which satisfy Eq. (6) is then as follows:

- (1) Select some value of $R_{bc} > R_{bc}^0$;
- (2) Calculate E_{el} and ∇E_{el} for this value of R_{bc} and for a small range of values of $R_{ab} > R_{ab}^0$. (Note that the roles of R_{bc} and R_{ab} in steps 1 and 2 may be interchanged);
- (3) Recalculate the right-hand side of Eq. (6) for each point \mathbf{R} (no assumption of equilibrium values) and find by interpolation the value of R_{ab} satisfying Eq. (6) for the given R_{bc} value;
- (4) Use the expression for $\partial E_{el}/\partial R_{ab}$ (or that for $\partial E_{el}/\partial R_{bc}$) to calculate $J(J+1)$ for this quasi-equilibrium. For example,

$$J(J+1) = I^2(\partial E_{el}/\partial R_{ab})/\hbar^2(M_{11}R_{ab} + M_{12}R_{bc}). \quad (7)$$

The total energy E for this value of $J(J+1)$ is then given by the sum of the nonrigid $E_r = \hbar^2 J(J+1)/2I$ and an interpolated value of E_{el} for the structure \mathbf{R} . The entire process is repeated to obtain as many values as desired for the rotational energy dispersion $E(J)$. The accompanying structures $\mathbf{R}(J)$ comprise a one-dimensional centrifugal distortion pathway, parametric in J , in the two-dimensional \mathbf{R} space.

If desired, one may calculate, as previously outlined (5), an effective J -dependent quartic constant $D(J)$ defined as the centrifugal stabilization energy $\Delta E = E(\text{rigid}) - E(\text{nonrigid})$ divided by $[J(J+1)]^2$. The limit of $D(J)$ as J approaches zero may be taken as the calculated D value for the molecule.

The ab initio calculations were carried out using the GAUSSIAN90 and -92 programs (26, 27) at the HF/6-31G** and CISD/6-31G** levels. Gradients were obtained analytically in both cases, while vibrational wavenumbers were obtained analytically in the HF case and numerically from analytic gradients in the CISD case. As a comparison CISD wavenumbers were also obtained numerically from second differences of the energy (with frozen cores). The wavenumbers are for reference only as they are not used explicitly in our procedure for calculating rotational energies outlined above, although their information content enters implicitly via the displacement dependence of the gradients.

The procedure as outlined above may appear to be cumbersome and computationally intensive. The yield, however, is much greater than a calculated quartic spectroscopic constant, namely one obtains both the dispersion $E(J)$ and the associated pathway $\mathbf{R}(J)$. If desired, a simplified but cruder calculation could be made by replacing $\mathbf{R}(J)$ in Eqs. (4) and (5) by its ($J=0$) equilibrium value $\mathbf{R}(0)$.

RESULTS

We first consider H^{12}CP , with Fig. 1 displaying the bond length changes ΔR_{CP} and ΔR_{CH} as a function of J . The former is 4 to 5 times larger than the latter, indicating that the light H atom "rides" along as the C-P bond stretches. The ΔR_{CP} values are larger at the CISD/6-31G** level than at the HF/6-31G** level for a given value of J , reflecting the smaller force constant and hence smaller vibrational wavenumber for the C-P stretch (Table I) at the former level.

From the interpolated solutions of Eq. (6) for a number of ΔR_{CP} values we obtain the effective quartic constants shown as a function of J in Fig. 2. The extrapolation of these values to $J=0$ gives the calculated quartic constants D listed in Table I. The extrapolation was made by assuming the linearity of $\Delta E/[J(J+1)]^2$ vs $J(J+1)$ for small J . The intercept yields the D value, while the negative of the slope, equivalent

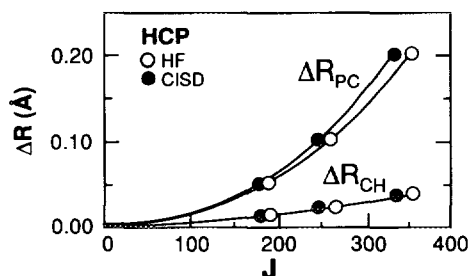


FIG. 1. Centrifugal displacements ΔR_{CH} and ΔR_{CP} in Å for $H^{12}CP$ as a function of the angular momentum quantum number J as obtained at the HF/6-31G** (open circles) and CISD/6-31G** (closed circles) levels.

to the negative of the curvature of $\Delta E/[J(J+1)]^2$ vs J , yields the sextic constant H . The CISD value of H (Table I) is approximately $9.6 \times 10^{-14} \text{ cm}^{-1}$, about 0.6 of the HF value and with a sign corresponding to a positive contribution to the rotational energy dispersion $E(J)$.

Our CISD value of D , namely $6.24 \times 10^{-7} \text{ cm}^{-1}$, while larger than our HF value of 5.94×10^{-7} , is still somewhat smaller than the observed value (13) of $7.025(17) \times 10^{-7} \text{ cm}^{-1}$, because our computed gradients rise too steeply with the displacements, equivalent to having (implicit) vibrational wavenumbers which are somewhat too large. The reported SCEP computed value (22) of $7.01 \times 10^{-7} \text{ cm}^{-1}$ is closer to the observed value as it is based on empirically adjusted quadratic potential energy function terms. Our CISD sextic coefficient H of $9.6 \times 10^{-14} \text{ cm}^{-1}$ is close to the SCEP value

TABLE I
Bond Lengths and Spectroscopic Constants for $H^{12}CP$

Constant*	HF/6-31G**	CISD/6-31G**	Observed
R(C-H)	1.063	1.066	1.0667(5) ^b
R(C-P)	1.515	1.536	1.5421(5) ^b
B	0.690	0.672	0.6632742(16) ^c
D	5.94×10^{-7}	6.24×10^{-7}	$7.025(17) \times 10^{-7}$ ^c
H	1.6×10^{-13}	9.6×10^{-14}	-----
ν_1	3578	3483 (3479) ^d	3216.89153(72) ^e
ν_2	830	749 (735) ^d	674.69914(45) ^e
ν_3	1472	1380 (1374) ^d	1278.2798(13) ^e

a) Bond lengths in Å, spectroscopic constants and wavenumbers in cm^{-1} .

b) Ref. (7).

c) Ref. (13).

d) CISD wavenumbers computed from first differences of analytic gradients (values in parentheses computed from second differences of CISD energies).

e) Ref. (12); from ref. (13) the harmonic wavenumber $\omega_2 = 687.867(3) \text{ cm}^{-1}$.

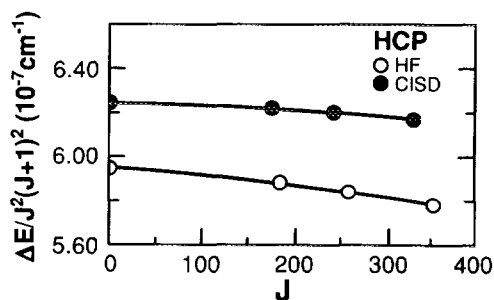


FIG. 2. Effective quartic constants $D(J)$ (centrifugal stabilization energies ΔE divided by $[J(J+1)]^2$ in 10^{-7} cm^{-1} for H^{12}CP as a function of the angular momentum quantum number J as obtained at the HF/6-31G** (open circles) and CISD/6-31G** (closed circles) levels. The points for $J=0$ were obtained by linear extrapolation of the effective constants as a function of $J(J+1)$.

of $1.001 \times 10^{-13} \text{ cm}^{-1}$, but being based on the slope of the centrifugal stabilization energy vs $J(J+1)$, is not very precisely determined.

To illustrate the contributions to the energy consider the CISD results for $\Delta R_{\text{CP}} = 0.05 \text{ \AA}$, for which J is approximately 178 (Fig. 1). This and other data points are admittedly for very high J as necessitated by the selection of displacements sufficiently large as to yield numerically significant gradients. The total energy for J of 178 is $20\,666 \text{ cm}^{-1}$, less by 624 cm^{-1} than the computed rigid rotor energy of $21\,290 \text{ cm}^{-1}$ for the same J value. This total energy consists of $20\,044 \text{ cm}^{-1}$ as “rotational energy” $BJ(J+1)$, where B is the effective rotational constant calculated at the quasi-equilibrium structure for the given J value, and 622 cm^{-1} as “electronic energy” defined as the change in the CISD energy accompanying the distortion. Stated differently, the centrifugal stabilization energy of 624 cm^{-1} arises from a 1246 cm^{-1} drop in the rotational energy balanced against the 622 cm^{-1} increase in electronic energy. The ratio of the magnitudes of these contributions to the stabilization energy is 2.003; in our study (6) of analytic classical rotational energy expressions for diatomic molecules we showed that this ratio for a harmonic oscillator (HO) is rigorously $(1+x)(2+x)$, where x is the reduced displacement $(r-r_e)/r_e$, with r_e being the equilibrium separation. Similarly for a Morse oscillator (MO) this ratio is $bx(1+x)(2+x)\exp(-bx)/(1-\exp(-bx))$, where x again is the reduced displacement and b is the dimensionless parameter $\beta r_e = (k/2D_e)^{1/2}r_e$. To order x the MO ratio equals $2 + (3-b)x$, which typically is much closer to 2 than is the HO ratio which to the same order is $2 + 3x$.

In Table II we present our CISD/6-31G** values for the quartic coefficient D and for the vibrational wavenumbers of the isotopic variants D^{12}CP , H^{13}CP , and D^{13}CP . The agreement with experiment (where available) and with the SCEP computed value (22) of D is comparable to that for H^{12}CP , namely both the computed D values and the wavenumbers are approximately 10% too large. Again it should be noted that the SCEP values are based in part on empirically adjusted force constants. The ratios of our computed D and wavenumber values for the isotopic variants to the values for H^{12}CP are in excellent agreement both with the SCEP and with the experimental ratios. A minor exception is the ratio of D values $\text{H}^{13}\text{CP}/\text{H}^{12}\text{CP}$; both our CISD and the SCEP values are a few percent higher than the observed ratio which is, we note, based on a fairly imprecise value of $6.33(21) \times 10^{-7} \text{ cm}^{-1}$ for H^{13}CP .

TABLE II
Spectroscopic Constants for HCP Isotopomers

Constant ^a	D ¹² CP	H ¹³ CP	D ¹³ CP	D ¹² CP/H ¹² CP	H ¹³ CP/H ¹² CP	D ¹³ CP/H ¹³ CP
D(10 ⁻⁷)						
This work	4.23	5.77	3.91	0.678	0.925	0.627
SCEP ^b	4.74	6.47	-----	0.676	0.923	-----
Obs.	4.76078 ^c	6.33 ^d	-----	0.678	0.901	-----
$\nu_1(\sigma)$						
This work	2604	3469	2581	0.748	0.996	0.741
Obs.	2419.42515 ^e	3205 ^d	-----	0.752	0.996	-----
$\nu_2(\pi)$						
This work	582	744	574	0.777	0.993	0.766
Obs.	525.220421 ^f	-----	-----	0.778	-----	-----
$\nu_3(\sigma)$						
This work	1321	1346	1294	0.957	0.975	0.938
Obs.	1231.40260 ^g	-----	-----	0.963	-----	-----

^a All values in cm⁻¹; our calculated values are at the CISD/6-31G** level.

^b Ref. (22); the similarly computed value for H¹²CP is 7.01×10^{-7} cm⁻¹. ^cRef. (17). ^dRef. (12). ^eRef. (15).

SUMMARY

In summary we have extended our theoretical method of employing analytic quantum chemical gradients for the calculation of the geometries and energies of centrifugally distorted molecules to the description of noncentrosymmetric linear triatomic molecules. The extension is illustrated by its application to the molecule HCP. In addition to obtaining quartic and sextic spectroscopic constants, we have obtained a centrifugal distortion pathway. This pathway may be described by the ratio $\Delta R_{CH}/\Delta R_{CP}$ of displacements; at the CISD/6-31G** level this ratio is approximately 0.23 for low J values, but decreases as J increases, indicating that the light H atom to a first approximation "rides" along as the C-P bond stretches. Thus the centrifugal displacement mode is dominated by the contribution from the C-P stretching mode, with a calculated wavenumber ν_3 of 1380 cm⁻¹ (Table I) at the CISD/6-31G** level; the observed value (12) is somewhat smaller, namely 1278.2798 cm⁻¹. This fundamental is associated with a computed ratio $\Delta R_{CH}/\Delta R_{CP}$ of 0.17, while the ratio for the higher wavenumber ν_1 mode (3483 cm⁻¹ at the CISD/6-31G** level) is quite different, namely -8.7 (note the sign). More specifically, the centrifugal displacement mode has an approximately 50% greater ratio $\Delta R_{CH}/\Delta R_{CP}$ than does the ν_3 normal mode.

The key results of this investigation are the following: first, a presentation of the detailed equations whose simultaneous solutions define the centrifugal distortion pathways for arbitrary linear molecules ABC; second, the application of these equations at the HF/6-31G** and CISD/6-31G** levels of electronic structure theory to the molecule HCP with a focus on the bond length changes and with a demonstration

that the light H atom to first approximation rides along with the heavier C atom; and third, extraction of quartic spectroscopic constants from the rotational energy dispersions for four isotopic variants of HCP.

ACKNOWLEDGMENT

The author thanks Research Systems of the Information Technology Division, University of Michigan, for the use of its computational facilities.

RECEIVED: March 16, 1993

REFERENCES

1. L. L. LOHR AND J.-M. POPA, *J. Chem. Phys.* **84**, 4196-4204 (1986).
2. L. L. LOHR AND A. J. HELMAN, *J. Comput. Chem.* **8**, 307-312 (1987).
3. L. L. LOHR, *Int. J. Quantum Chem., Quantum Chem. Symp.* **21**, 407-415 (1987).
4. A. TALEB-BENDIAB AND L. L. LOHR, *J. Mol. Spectrosc.* **132**, 413-421 (1988).
5. L. L. LOHR, *J. Mol. Struct. THEOCHEM.* **99**, 265-270 (1989).
6. L. L. LOHR, *J. Mol. Spectrosc.* **155**, 205-214 (1992).
7. J. K. TYLER, *J. Chem. Phys.* **40**, 1170-1171 (1964).
8. J. W. C. JOHNS, H. F. SHURVELL, AND J. K. TYLER, *Can. J. Phys.* **47**, 893-920 (1969).
9. J. W. C. JOHNS, J. M. R. STONE, AND G. WINNEWISSER, *J. Mol. Spectrosc.* **38**, 437-440 (1971).
10. J.-M. GARNEAU AND A. CABANA, *J. Mol. Spectrosc.* **69**, 319-325 (1978).
11. J.-M. GARNEAU AND A. CABANA, *J. Mol. Spectrosc.* **79**, 502-506 (1980).
12. J.-M. GARNEAU AND A. CABANA, *J. Mol. Spectrosc.* **87**, 490-505 (1981).
13. A. CABANA, Y. DOUCET, J.-M. GARNEAU, C. PÉPIN, AND P. PUGET, *J. Mol. Spectrosc.* **96**, 342-350 (1982).
14. J. LAVIGNE AND A. CABANA, *Can. J. Phys.* **60**, 304-306 (1982).
15. J. LAVIGNE, C. PÉPIN, AND A. CABANA, *J. Mol. Spectrosc.* **99**, 203-208 (1983).
16. J. LAVIGNE, C. PÉPIN, AND A. CABANA, *J. Mol. Spectrosc.* **104**, 49-58 (1984).
17. C. PÉPIN AND A. CABANA, *J. Mol. Spectrosc.* **119**, 101-106 (1986).
18. K. K. LEHMANN, S. C. ROSS, AND L. L. LOHR, *J. Chem. Phys.* **82**, 4460-4469 (1985).
19. Y.-T. CHEN, D. M. WATT, R. W. FIELD, AND K. K. LEHMANN, *J. Chem. Phys.* **93**, 2149-2151 (1990).
20. M. A. MASON AND K. K. LEHMANN, *J. Chem. Phys.* **98**, 5184-5190 (1993).
21. S. C. ROSS AND P. R. BUNKER, *J. Mol. Spectrosc.* **101**, 199-211 (1983).
22. P. BOTSCHWINA AND P. SEBALD, *J. Mol. Spectrosc.* **100**, 1-23 (1983).
23. P. BOTSCHWINA, *Chem. Phys.* **81**, 73-85 (1983).
24. J. E. BLOOR AND J. YU, *J. Phys. Chem.* **94**, 5586-5589 (1990).
25. E. GOLDSTEIN, Y. JIN, M. R. CARILLO, AND R. J. CAVE, *J. Comput. Chem.* **14**, 186-194 (1993).
26. M. J. FRISCH, M. HEAD-GORDON, G. W. TRUCKS, J. B. FORESMAN, H. B. SCHLEGEL, K. RAGHAVACHARI, M. ROBB, J. S. BINKLEY, C. GONZALEZ, D. J. DEFREES, D. J. FOX, R. A. WHITESIDE, R. SEEGER, C. F. MELIUS, J. BAKER, R. L. MARTIN, L. R. KAHN, J. J. P. STEWART, S. TOPIOL, AND J. A. POPLE, "GAUSSIAN90," Revision I, Gaussian, Inc., Pittsburgh PA, 1990.
27. M. J. FRISCH, G. W. TRUCKS, M. HEAD-GORDON, P. M. W. GILL, M. W. WONG, J. B. FORESMAN, B. G. JOHNSON, H. B. SCHLEGEL, M. A. ROBB, E. S. REPLOGLE, R. GOMPERS, J. L. ANDRES, K. RAGHAVACHARI, J. S. BINKLEY, C. GONZALEZ, R. L. MARTIN, D. J. FOX, D. J. DEFREES, J. BAKER, J. J. P. STEWART, AND J. A. POPLE, "GAUSSIAN92," Revision A, Gaussian, Inc., Pittsburgh, PA, 1992.