Molecular Orbital Constraint of Interaction Coordinates. An Approximate Quadratic Potential Function

B. I. Swanson,* T. H. Arnold, M. J. S. Dewar, J. J. Rafalko, H. S. Rzepa, and Y. Yamaguchi

Contribution from the Chemistry Department, University of Texas, Austin, Texas 78712. Received May 2, 1977

Abstract: An approximate method has been developed to calculate completely general quadratic potential functions using a combination of molecular orbital calculations and limited vibrational data. In the MOCIC (molecular orbital constraint of interaction coordinates) method, valence or symmetry interaction displacement coordinates evaluated using SCF–MO calculations are constrained in a subsequent determination of the quadratic compliance constants. The only experimental data required in the MOCIC method are the fundamental frequencies of vibration. MOCIC potential functions have been evaluated for several small molecules of high symmetry using the semiempirical molecular orbital scheme MNDO (modified neglect of diatomic overlap). The potential functions obtained using MOCIC are in remarkable agreement with those functions uniquely obtained using extensive vibrational data. Comparison of MOCIC functions with both MNDO and ab initio SCF–MO potential functions shows a significant improvement in both primary and interaction constants. The MOCIC functions also exhibit a substantial improvement in calculating auxiliary data, particularly centrifugal distortion constants.

Introduction

The paucity of vibrational data in the evaluation of completely general quadratic potential functions is well known.[1-3] In spite of the increased use of auxiliary data (isotopic frequency shifts, Coriolis coupling constants, centrifugal distortion constants, and amplitudes of vibration) unique general quadratic potential functions have been obtained only for a limited number of high-symmetry small molecules. It is striking to note that even for relatively simple molecules (for example, $Co(CO)_3NO$[4] and C_2H_6[5]) where there are many pieces of vibrational data, unique force fields cannot be obtained. The high correlation among force (or compliance) constants often prevents a simultaneous least-squares determination of all of the unique quadratic constants.

Attempts to obviate the problem of limited data have not been particularly successful. Those interested in unique quadratic functions often resort to using judicious prior constraints of certain constants.[1-3] Quite often it is assumed that certain interaction constants are zero. Alternatively, interaction and/or primary constants are simply transferred from similar molecules for which these constants are known. The principal difficulty encountered in transferring constants is that there are not enough molecules for which all of the constants are known.

The various approximate force fields which have been developed over the years[6-11] represent a severe form of establishing prior constraints. Many of these approximate methods are based on constraints established through bonding considerations, and are found to work reasonably well for limited systems. Unfortunately, none of the existing approximate methods can be reliably used on a wide variety of molecules.

One encouraging development in recent years has been the use of SCF–MO methods to evaluate potential functions.[12-16] The ab initio molecular orbital approach works extremely well for cubic and quartic force constants,[17] while often overestimating the quadratic constants. However, it has been shown that the quadratic constants may be improved significantly by scaling the primary force constants to the observed data.[15,16] One limitation of this approach is that ab initio calculations can only be carried out for relatively simple systems at present.

In this report we explore an approximate method based on the combined use of MO calculations and limited vibrational data (the fundamental frequencies of vibration for the normal isotopic species). This new method, which we have termed

molecular orbital constraint of interaction coordinates (MOCIC), is couched in the language of compliance constants[18-20] rather than the usual force constants.[21] MOCIC relies on the prior constraint of interaction displacement coordinates,[22] determined using SCF–MO techniques, in a least-squares evaluation of the complete compliant field. The suggestion that MO calculations be used to establish constraints on interaction coordinates in the evaluation of quadratic potential functions is not new. In 1970 Jones and Ryan[23] suggested such an approach in dealing with potential functions which are not uniquely determinable from existing data. In this report we stress the use of the recently developed[24] semiempirical SCF–MO scheme MNDO (modified neglect of diatomic overlap).[25]

The MOCIC Method

In the compliance constant formalism, which has been discussed extensively in the literature as a useful alternative to the usual **GF** method,[1,18-20,23,27] the potential energy is given by

$$V = \frac{1}{2} \sum_{ij} C_{ij} \, \mathcal{F}_i \, \mathcal{F}_j \tag{1}$$

where $\mathcal{F}_i$ is a general force along internal coordinate R_i. The problem here is to obtain best estimates of the various compliants, C_{ij}, which will satisfy the secular equation

$$CKL = L\Lambda^{-1} \tag{2}$$

C is the compliance constant matrix ($C = F^{-1}$), K the kinetic energy matrix, L the usual eigenvector matrix in the **GF** formalism, and Λ^{-1} a diagonal eigenvalue matrix with elements $\lambda_i = \frac{1}{4}\pi^2\nu_i{}^2$. For the molecules dealt with in this report the vibrationally determined compliance functions have been obtained from available general vibrational force fields. Comparison of the compliance functions obtained using MOCIC with those obtained from vibrational data will provide one criterion for the reliability of the MOCIC method.

The valence interaction displacement coordinate $(i)_j$ is defined as the change in coordinate R_i required to minimize the potential energy following a fixed distortion in R_j.[1,22] The direct relationship between $(i)_j$ and the interaction compliants $((i)_j = C_{ij}/C_{jj})$ provides the basis for the constraint in the MOCIC method. The constraint of the various $(i)_j$ fixes the ratio of interaction to primary compliants, thereby reducing

the number of refinable parameters to the number of unique primary compliance constants.

In our original approach,[28] the various $(i)_j$ were evaluated from MO calculations by geometry optimization based on the minimization of energy. First, the lowest energy configurations of a molecule were evaluated for a series of fixed distortions of R_j from its equilibrium value. The change in coordinate R_i as a function of R_j near equilibrium then provides an estimate of $(i)_j$. The interaction displacement coordinates may be more easily obtained by simply evaluating the quadratic force field for the molecule in its equilibrium configuration. The molecular orbital force matrix is inverted and the quadratic compliants so obtained are used to evaluate the interaction displacement coordinates. The two approaches are equivalent. The latter method was employed here primarily because less computer time is required to obtain F from the MO calculation than to evaluate $(i)_j$ via geometry optimization.

The various $(i)_j$ obtained from the molecular orbital calculation, along with the fundamental frequencies of vibration, provide the input for the evaluation of C using the compliance constant perturbation program COMPLY.[29] For the molecules studied here harmonic frequencies have been employed, except for CF_4 and NF_3. The actual constraint of $(i)_j$ may be effected by carrying out the refinement in terms of symmetry compliance constants using the Z matrix.[28] The only refinable parameters are the primary valence compliants.

Symmetry Interaction Displacement Coordinate Constraint. In the foregoing discussion the valence interaction displacement coordinates were constrained in evaluating C. Alternatively, the symmetry interaction coordinates

$$(i)_j{}^s = C_{ij}{}^s/C_{jj}{}^s \tag{3}$$

may be constrained in an evaluation of C. Here $(i)_j{}^s$ gives the change in symmetry coordinate S_i required to minimize the energy following a unit distortion of S_j: $C_{ij}{}^s$ and $C_{jj}{}^s$ are symmetry compliants. Using the symmetry constraint approach the refinable parameters become the primary symmetry compliants, $C_{jj}{}^s$. There will generally be more observables than parameters using valence constraints, since the number of fundamental frequencies usually exceeds the number of unique primary valence compliants. On the other hand, using symmetry constraints the observable to refinable parameter ratio will be unity.

There are two advantages to the symmetry constraint approach. First, it is much easier to apply selective constraints of a few interaction compliants using symmetry constraints. The application of selected constraints using MOCIC would become useful for a molecule where there are not quite enough data, or the right kind, to allow a unique determination of C directly. In effect, one or more symmetry blocks may be determinable from existing data and constraints will only be required for certain symmetry $C_{ij}{}^s$'s.

The second advantage is that the potential functions obtained using symmetry constraints appear to fit the data better than those obtained using valence constraints. Admittedly, this statement is based on a limited number of molecules. The potential functions for the molecules discussed here were determined using both methods. In all but one case the symmetry constraint approach yielded significantly better compliance functions (see below). For CF_4 the refinement based on valence constraints yielded essentially the same function as that based on symmetry constraints. The compliance functions obtained using both valence and symmetry constraints are presented in the tables for comparison.

In both the valence and symmetry constraint approaches there is an ambiguity concerning which combination of primary compliants and interaction displacement coordinates should be used to define the interaction compliance constants.

This problem is easily handled in the symmetry method by the following averaging procedure, $C_{ij}{}^s = \frac{1}{2}[(i)_j{}^s \, C_{jj}{}^s + (j)_i{}^s \, C_{ii}{}^s]$.

This simplicity is lost for the valence constraints since $C_{ij}{}^s$ are equal to linear combinations of the valence compliants. Because of the complexity, it is difficult to apply a generalized averaging scheme. Approaching the problem empirically, whenever a constraint could be made in more than one way, we calculated the potential functions for each constraint. This case occurs in constraining a stretch–bend interaction displacement coordinate where one could use either the primary stretching or primary bending constant. For the molecules studied we found that scaling to the primary stretch compliant gave slightly better results for the fit between observed and calculated data. Thus, results reported here are based on a stretch–stretch scaling for the stretch–bend interaction coordinates. For those molecules where there is a possible ambiguity as regards stretch–stretch or bend–bend interaction displacement coordinates, we found that the final potential functions were practically insensitive to the primary constant used in scaling. Nonetheless, the particular primary constant used in each constraint will be indicated in the tables.

MNDO Force Constants. The MNDO method has been described in detail.[24] After the geometry of each molecule had been determined by minimizing the total energy with respect to all geometrical variables, the force constants were calculated using the force method.[12-16] The first derivatives of the total energy with respect to the ith Cartesian coordinate were calculated analytically[31] using the newly obtained wave functions. Their self-consistency is at least 10^{-8} for the standard deviation of bond orders for the jth distorted Cartesian coordinates ($X_j = X_j{}^0 + \Delta X_j$ and $X_j = X_j{}^0 - \Delta X_j$, where X_j is the jth coordinate at optimized geometry). The increment ΔX_j was normally taken to be 0.001 Å. The ijth elements of the Cartesian force constant matrix were evaluated by the finite difference method:

$$(F_x)_{ij} = \frac{\left(\dfrac{\partial E_{total}}{\partial X_i}\right)_{X_j{}^0 + \Delta X_j} - \left(\dfrac{\partial E_{total}}{\partial X_i}\right)_{X_j{}^0 - \Delta X_j}}{2\Delta X_j} \tag{4}$$

As a result of round-off error, the elements of F_x had to be averaged ($[(F_x)_{ij} + (F_x)_{ji}]/2$) to obtain a symmetric matrix. The usual transformation from Cartesian to internal coordinates was made using the B matrix.[32]

Results and Discussion

The general quadratic compliance functions for the molecules studied in this report are well known from existing vibrational data. Accordingly, there are several comparisons which provide information on the reliability of the MOCIC approach. The most important comparison is that of the potential constants themselves. For most of the molecules studied, auxiliary data, including Coriolis and centrifugal distortion constants, are well known from experiment. Thus, there exists a surfeit of experimental data, not included in the actual MOCIC determination of potential functions, which provide some measure of MOCIC's reliability.

Clearly, we have to evaluate how well MOCIC does in relationship to other approximate methods. We have relied on a comparison with SCF–MO potential functions, as these are the best approximate methods to date. The obvious comparison of the MOCIC–MNDO function with that function obtained using MNDO alone is a crucial test of the merit of the MOCIC concept. If the MOCIC–MNDO function does not significantly improve the MNDO function there is no point in applying the MOCIC approach. An equally important comparison is that of the MOCIC–MNDO functions with ab initio

Table I. Water

| | Vib[a] spect | SCF–MO functions[b] | | | MOCIC functions[e] | | |
| | | MNDO | Ab initio | | Symmetry[f] constraint | | Valence[f] constraint |
			Unscaled[c]	Scaled[d]	MNDO	Ab initio	MNDO
C_r[g]	0.119	0.109	0.108	0.120	0.120	0.120	0.119
F_r	8.454	9.257	9.372	8.452	8.454	8.454	8.470
C_α	1.338	0.948	1.239	1.333	1.337	1.337	1.338
C_{rr}	0.002	−0.002	0.003	0.003	0.003	0.003	−0.002
$C_{r\alpha}$	−0.037	−0.033	−0.039	−0.048	−0.042	−0.043	−0.036
T_{aaaa}[h]	2.67	1.97	2.49	2.72	2.70	2.70	
T_{bbbb}	0.93	0.68	0.84	0.90	0.91	0.91	
T_{aabb}	−1.06	−0.70	−0.98	−1.04	−1.05	−1.05	
D_2O p[i]	0	162	115	1.5	0.5	0.5	35

[a] K. Kutchitsu and L. S. Bartell, *J. Chem. Phys.*, **36**, 2460 (1962). [b] All of the SCF–MO functions were evaluated with the gradient method. [c] Reference 33. This is the source for MOCIC. [d] Reference 16c. [e] The MOCIC potential functions were refined with the experimental frequencies of the normal isotope and the interaction displacement coordinates fixed to the SCF–MO values. [f] The symmetry constraint consists of 1 $(i)_j{}^s$ (see text) while $(r)_r$ and $(\alpha)_r$ are constrained in the valence method. [g] All compliance constants are in Å/mdyn. The F_r are in mdyn/Å. [h] The units are in Å/mdyn. See the right side of eq 1 in H. Takeo, E. Hirota, and Y. Morino, *J. Mol. Spectrosc.*, **34**, 370 (1970). [i] $p = (\Sigma_{i=1}^{n}|\Delta\omega_i|)/n$, where $|\Delta\omega|$ is the observed − calculated frequency difference in cm^{-1} and n is the number of frequencies.

SCF–MO functions. Fortunately, for several of the systems studied here (H_2O,[16,33] NH_3,[34] CH_4,[35] NF_3,[36] and C_2H_4[37]) ab initio SCF–MO calculations are available; these have been labeled "ab initio" in the tables. It should be noted that the ab initio SCF–MO function for NF_3 was evaluated using a minimum basis set (5s/2p).[36] Certainly, this does not represent the state of the art as regards ab initio SCF–MO methods and, no doubt, a better ab initio SCF–MO function for NF_3 will be obtained in the future.

In principle, any MO scheme may be used in the MOCIC approach. We have also evaluated potential functions using the ab initio force fields as a starting point for MOCIC treatments; these are labeled "MOCIC–ab initio" in the tables.

The most important point to emerge from Tables I–VIII is that MOCIC functions, both MOCIC–MNDO and MOCIC–ab initio, are in remarkable agreement with the vibrational functions. A comparison of MOCIC–MNDO and MNDO functions reveals that the MOCIC approach significantly improves the initial MNDO compliance functions for all of the molecules studied here. The improvement in the primary constants is dramatic; note particularly the stretching constants. MNDO consistently underestimates the primary stretching compliance constants (overestimates the corresponding primary force constants; see Tables I–VIII). In the cases of NF_3, CH_3F, and CF_4 the M–F stretching force constants determined using MNDO alone are 3.0, 2.2, and 1.6 times as great as their vibrationally determined counterparts. Even for these extreme cases, the MOCIC–MNDO primary constants are essentially the same as those obtained by experiment. Close agreement between the primary constants was expected since the most important feature of the MOCIC approach is that it scales the primary constants to the observed frequencies. The improvement in the primary compliance and force constants in using the MOCIC approach is also manifested in the better fit between the observed and calculated data for isotopes not included in the refinements (p in Tables I–VIII). A comparison of ab initio and MOCIC–ab initio functions also reveals a consistent, though not as large, improvement using MOCIC.

The interaction compliants evaluated using MOCIC are also in close agreement with those obtained experimentally. For example, in the MOCIC–MNDO functions, the signs of only a few interaction compliants (i.e., the deformation–deformation interaction in C_2H_7) are miscalculated. In the case of the MOCIC–ab initio functions all of the signs are correctly evaluated except one. The magnitudes of the more important

Table II. Boron Trifluoride

| | Vib[a] spect | MNDO | MOCIC functions[b] | |
			Symmetry[c] constraint MNDO	Valence[c] constraint MNDO
C_r	0.139	0.091	0.140	0.138
F_r	7.552	11.489	7.531	7.655
C_α	1.321	1.265	1.316	1.353
C_{rr}	−0.015	−0.010	−0.015	−0.015
$C_{r\alpha}$[d]	−0.037	−0.028	−0.037	−0.043
$C_{\alpha\alpha}$	−0.660	−0.632	−0.658	−0.677
$^{11}BF_3$ p[e]	0.3	185	0.5	1.0
Z[f]	0.00	0.04	0.00	0.02

[a] Reference 28. [b] The MOCIC functions were calculated with the frequencies of $^{10}BF_3$. [c] See footnote f, Table I. [d] $C_{r\alpha}$ describes the interaction between a bond stretch with an adjacent angle. [e] See footnote i, Table I. [f] Z is $(\Sigma_{i=3}^{4}|\zeta_{ii}$ (obsd) $- \zeta_{ii}$ (calcd)$|)/2$. All ζ's are dimensionless.

interaction compliance are all estimated quite well by the MOCIC functions.

If the MOCIC approach is to have any utility, the SCF–MO scheme that is used to establish the constraints of the interaction displacement coordinates must be capable of obtaining accurate estimates of the various $(i)_j$. MNDO underestimates both the primary stretch and stretch–stretch interaction compliants. However, the $(i)_j$'s are estimated properly since the accumulated errors in both C_{jj} and C_{ij} are reduced in taking the ratio C_{ij}/C_{jj}.

Since MNDO evaluates interaction displacement coordinates more accurately than the corresponding interaction compliants, it is not surprising that MOCIC–MNDO interaction compliants provide at least as good, and in many instances better, estimates of the vibrational C_{ij}'s than the corresponding MNDO values. Those bend–bend interaction compliants with large values are most favorably improved (for example, $C_{\alpha\alpha'}$ and $C_{\alpha\alpha''}$ for CH_4 and $C_{\alpha\alpha}$ for NH_3). The improvement in the stretch–stretch interaction constants using MOCIC, while not as great in magnitude, is no less important. It should be noted, however, that while the symmetry constraint approach showed improvement over MNDO as regards interaction compliants, the valence approach did not. Similar improvements are noted in using the MOCIC approach on the ab initio functions suggesting that ab initio SCF–MO calculations also estimate interaction displacement coordinates

Table III. Trifluoroamine

| | Vib[a] spect | SCF–MO functions | | MOCIC functions[c] | | |
| | | | | Symmetry[f] constraints | | Valence[f] constraints |
		MNDO	Ab initio[b]	MNDO	Ab initio	MNDO
C_r	0.265	0.094	0.092	0.255	0.271	0.231
F_r	4.164	11.58	11.23	4.519	4.078	4.888
C_α	1.019	0.818	0.982	1.079	0.993	1.172
C_{rr}	−0.042	−0.012	−0.005	−0.047	−0.044	−0.029
$C_{r\alpha'}{}^e$	0.047	0.022	0.013	0.048	0.037	0.054
$C_{r\alpha}{}^e$	−0.061	−0.037	−0.030	−0.073	−0.056	−0.090
$C_{\alpha\alpha}$	−0.128	−0.109	−0.108	−0.100	−0.118	−0.156
${}^{15}NF_3 \, p^d$	0	322	276	1	0	34
${}^{14}NF_3 \, T^g$	0.5	6.5	4.0	0.0	1.0	

[a] A. Allen, J. L. Duncan, J. H. Holloway, and D. C. McKean, *J. Mol. Spectrosc.*, **31**, 368 (1969). [b] Reference 36. [c] The anharmonic frequencies of ${}^{14}NF_3$ (see *a*) were used in the MOCIC refinements. [d] See footnote *i*, Table I. [e] $C_{r\alpha'}$ involves the interaction between an angle and a stretching coordinate which does not define the angle whereas for $C_{r\alpha}$ the stretching coordinate is adjacent to the angle. [f] The symmetry constraint consists of $2(i)_j{}^s$ while $(r)_r$, $(\alpha)_r$, $(\alpha')_r$, and $(\alpha)_\alpha$ are constrained in the valence method. [g] T is $(|\Delta D_J| + |\Delta D_{JK}|)/2$. Dimension is kHz and accuracy ±0.25 kHz.

Table IV. Ammonia

| | Vib[a] spect | SCF–MO functions | | MOCIC functions[c] | | |
| | | | | Symmetry[d] constraint | | Valence[d] constraint |
		MNDO	Ab initio[b]	MNDO	Ab initio	MNDO
C_r	0.152	0.143	0.139	0.146	0.146	0.146
F_r	7.050	7.193	7.378	7.027	7.024	6.978
C_α	1.756	1.219	1.531	1.769	1.768	1.727
C_{rr}	0.009	−0.002	0.002	0.002	0.001	−0.002
$C_{r\alpha'}{}^e$	−0.057	−0.006	−0.016	−0.019	−0.020	−0.006
$C_{r\alpha}{}^e$	−0.095	−0.045	−0.050	−0.063	−0.056	−0.046
$C_{\alpha\alpha}$	0.243	−0.020	0.145	0.256	0.257	−0.028
p^f	4	134	61	13	13	75
$ND_3 \, T^g$	0.00	0.45	0.30	0.16	0.16	
Z^h	0.01	0.00	0.01	0.01	0.01	

[a] J. L. Duncan and I. M. Mills, *Spectrochim. Acta*, **20**, 523 (1964). [b] Reference 34. [c] The ${}^{14}NH_3$ frequency data were used as input. [d] See footnote *f*, Table III. [e] See footnote *e*, Table III. [f] See footnote *i*, Table I. [g] $T = |D_J \text{ (obsd)} - D_J \text{ (calcd)}|$; the dimension is 10^{-4} cm^{-1}. [h] Z is $|\zeta_{33} \text{ (obsd)} - \zeta_{33} \text{ (calcd)}|$.

Table V. Methane

| | Vib[a] spect | SCF–MO functions | | MOCIC functions[c] | | |
| | | | | Symmetry[d] constraint | | Valence[d] constraint |
		MNDO	Ab initio[b]	MNDO	Ab initio	MNDO
C_r	0.185	0.167	0.186	0.186	0.184	0.189
F_r	5.498	6.145	5.431	5.513	5.495	5.457
C_α	1.797	1.768	1.612	1.800	1.796	1.708
C_{rr}	−0.004	−0.007	−0.002	−0.005	−0.004	−0.008
$C_{r\alpha}{}^e$	−0.030	−0.037	−0.026	−0.041	−0.028	−0.041
$C_{\alpha\alpha'}{}^f$	−0.343	−0.397	−0.310	−0.343	−0.343	−0.383
$C_{\alpha\alpha''}{}^f$	−0.425	−0.182	−0.371	−0.429	−0.424	−0.176
$CD_4 \, p^g$	0	108	42	3	0	58

[a] See footnote *a*, Table IV. [b] Reference 35. [c] The ${}^{12}CH_4$ frequencies of footnote *a* were used. [d] The symmetry constraint consists of 1 $(i)_j{}^s$ while $(r)_r$, $(\alpha)_r$, $(\alpha')_\alpha$, and $(\alpha'')_\alpha$ are constrained in the valence method. [e] $C_{r\alpha}$ describes the interaction of a bond stretch with an adjacent angle. [f] $C_{\alpha\alpha'}$ describes the interaction of two angles which share a common bond coordinate. For $C_{\alpha\alpha''}$ the angles do not have a common bond coordinate. [g] See footnote *i*, Table I.

(particularly $(i)_j{}^s$) better than interaction compliants.

A comparison of MOCIC–MNDO and ab initio functions shows that for these molecules MOCIC–MNDO provides better estimates of the primary compliants in all cases. Certainly, this is encouraging as regards the general applicability of the MOCIC–MNDO method. In some instances MOCIC–ab initio does slightly better than MOCIC–MNDO.

One of the most important failings of approximate force field methods, which do not rely on SCF–MO calculation, is their inability to reproduce auxiliary data such as Coriolis coupling and centrifugal distortion constants. The MOCIC functions

Table VI. Carbon Tetrafluoride

| | | | MOCIC functions[b] | |
	Vib[a] spect	MNDO	Symmetry[c] constraint MNDO	Valence[c] constraint MNDO
C_r	0.16	0.10	0.17	0.16
F_r	6.97	11.45	6.77	7.31
C_α	1.03	1.04	1.00	1.06
C_{rr}	−0.02	−0.01	−0.02	−0.02
$C_{r\alpha}$[d]	−0.05	−0.04	−0.05	−0.06
$C_{\alpha\alpha'}$[e]	−0.23	−0.24	−0.24	−0.24
$C_{\alpha\alpha''}$	−0.09	−0.08	−0.06	−0.08
$^{13}CF_4\, p$[f]	0	150	1	7

[a] J. L. Duncan and I. M. Mills, *Spectrochim. Acta,* **20,** 1089 (1964). [b] The input data were the $^{12}CF_4$ frequencies from *a.* [c] See footnote *d,* Table V. [d] See footnote *e,* Table V. [e] See footnote *f,* Table V. [f] See footnote *i,* Table I.

Table VII. Methyl Fluoride

| | | SCF–MO functions | MOCIC functions[b] |
	Vib[a] spect	MNDO	Symmetry constraint[c] MNDO
C_R[d]	0.196	0.094	0.195
F_R	5.692	11.522	5.603
C_r	0.192	0.176	0.193
F_r	5.267	5.885	5.343
C_α[e]	1.674	1.762	1.659
C_β	1.212	1.140	1.241
C_{rR}	−0.004	−0.009	−0.014
C_{rr}	0.001	−0.008	−0.002
$C_{R\alpha}$	0.075	0.041	0.063
$C_{R\beta}$	−0.078	−0.043	−0.066
$C_{r\alpha}$[f]	0.042	0.044	0.043
$C_{r\beta}$[f]	−0.038	−0.035	−0.038
$C_{r\alpha'}$[f]	−0.002	−0.032	−0.033
$C_{r\beta'}$[f]	−0.001	0.029	0.031
$C_{\alpha\alpha}$	−0.428	−0.481	−0.417
$C_{\beta\beta}$	−0.129	−0.103	−0.139
$C_{\alpha\beta}$[g]	−0.450	−0.366	−0.380
$C_{\alpha\beta'}$[g]	−0.594	−0.617	−0.636
p[h]	3	149	24
$^{12}CD_3F\, T$[i]	0.0	0.5	0.1
Z[j]	0.01	0.10	0.11

[a] J. L. Duncan, D. C. McKean, and G. K. Speirs, *Mol. Phys.,* **24,** 553 (1972). [b] The refinements were carried out with the $^{12}CH_3F$ data from footnote *a.* Since the system was ill-conditioned with the raw MNDO force constants, the initial C_{22} was reduced to 1.4 Å/mdyn. [c] The symmetry constraint consists of $6(i)_j^s$. [d] R is the C–F stretching coordinate while r is a C–H coordinate. [e] α is a H–C–H angle and β is a F–C–H angle. [f] For $C_{r\alpha'}$ and $C_{r\beta}$ the stretching coordinates include the angles, but for $C_{r\alpha}$ and $C_{r\beta'}$ the stretching coordinates are not included in the angles. [g] $C_{\alpha\beta}$ describes the interaction of two angles which do not have a common bond coordinate. For $C_{\alpha\beta'}$ the angles share a common bond coordinate. [h] See footnote *i,* Table I. [i] $T = |D_J$ (obsd) $- D_J$ (calcd)$|$; the dimension is 10^{-6} cm^{-1}. [j] Z is $(\Sigma_{i=4}^6 |\zeta_{ii}$ (obsd) $- \zeta_{ii}$ (calcd)$|)/3$.

do a creditable job of reproducing such auxiliary data (Tables I–VIII). The agreement between observed and calculated data for Coriolis and centrifugal distortions constants using either MOCIC functions is excellent. In some instances, the fit between observed and calculated values is better for the MOCIC functions than for the experimentally determined compliant functions!

It is also evident from the tables that the MOCIC potential functions reproduce the auxiliary data better than the SCF–MO functions. There is a consistent, although small, improvement in Coriolis data. The improvement in the centrifugal distortion constants is quite substantial, particularly for those compounds where the SCF–MO functions underestimate the primary compliant. For example, the improvement in CH_3F, NF_3, and H_2O distortion constants is dramatic, while for NH_3 there is only slight improvement. The reason for this disparate improvement for certain auxiliary data is simply that Coriolis data depend more on interaction compliants, while centrifugal distortion constants are more heavily dependent on the primary constants. The SCF–MO methods predict Coriolis data better than they do distortion constants. This indicates that a scaling procedure like MOCIC is capable of substantially improving SCF–MO estimates of distortion data.

The results presented here suggest that MOCIC can provide useful approximate potential functions. However, these results are limited to small molecules of relatively high symmetry where few constraints are required in the MOCIC approach. The rationale for the selection of this admittedly limited basis set is simply that unique experimentally determined functions are available for these molecules. Clearly, it will be important to determine how well MOCIC–MNDO does on larger low-symmetry species. Unfortunately, it will become increasingly difficult to delineate how well MOCIC does on the more complex molecules if there are no reliable experimentally known functions for these molecules. Perhaps the best criterion for these larger molecules will be how well MOCIC reproduces auxiliary data. It will also be important to study molecules exhibiting a high degree of mixing of internal coordinates among the normal modes. In this regard it is encouraging that MOCIC–MNDO does so well on BF_3 where the interaction potential constants are quite large.

The MOCIC approach has potential utility in two types of problems. First, for those large molecules where there is no chance of defining an experimental function, MOCIC may provide a reasonable estimate of the potential constants. Certainly the low computer time requirements for MNDO ensure that MOCIC–MNDO can be applied to a large general class of molecules. The advantage of being able to obtain re-
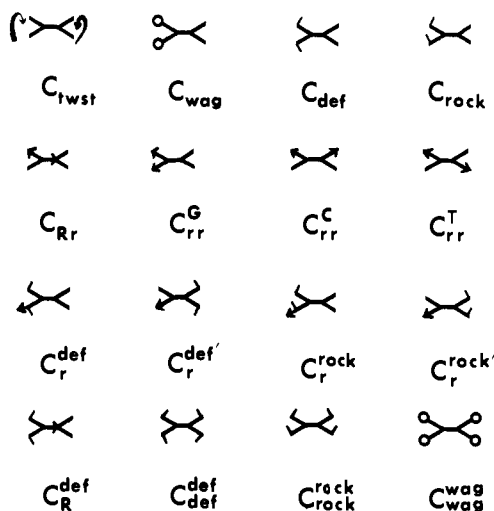

Figure 1. Internal coordinates for ethylene.

liable estimates of potential functions for large molecules is obvious. Certainly, reasonable estimates of Coriolis coupling and centrifugal distortion constants as well as mean square amplitudes of vibrations should be helpful in microwave, high-resolution infrared, and electron diffraction experiments. MOCIC may also prove useful in establishing selective constraints for a vast number of molecules for which there is considerable vibrational data, but not enough to allow a unique determination of the quadratic potential field.

Table VIII. Ethylene

	Vib[a] spect	SCF–MO function		MOCIC function Symmetry constraint[c]	
		MNDO	Ab initio[a,b]	MNDO	Ab initio
$C_R{}^d$	0.109	0.087	0.103	0.104	0.112
F_R	9.395	11.953	9.939	10.056	9.129
C_r	0.181	0.158	0.170	0.181	0.180
F_r	5.598	6.455	5.911	5.640	5.598
C_{lwsl}	1.548	2.219	1.290	1.547	1.547
C_{wag}	1.239	0.952	0.990	1.241	1.241
C_{def}	2.542	2.575	2.148	2.648	2.514
C_{rock}	2.157	2.264	1.940	2.173	2.159
C_{rR}	−0.003	−0.006	−0.002	−0.007	−0.002
$C_{rr}{}^g$	−0.003	−0.008	0.001	−0.003	−0.002
$C_{rr}{}^c$	0.000	0.000	−0.001	0.000	0.000
$C_{rr}{}^f$	0.000	0.000	0.001	−0.001	0.000
$C_r{}^{\text{def}}$	−0.011	−0.045	−0.032	−0.050	−0.035
$C_r{}^{\text{def}'}$	0.029	0.000	0.006	0.000	0.007
$C_r{}^{\text{rock}}$	−0.024	−0.108	−0.046	−0.111	−0.050
$C_r{}^{\text{rock}'}$	0.096	0.001	0.012	−0.003	0.013
$C_R{}^{\text{def}}$	0.075	0.089	0.066	0.101	0.075
$C_{\text{def}}{}^{\text{def}}$	−0.071	−0.047	−0.073	0.036	−0.096
$C_{\text{rock}}{}^{\text{rock}}$	0.293	0.155	0.313	0.302	0.309
$C_{\text{wag}}{}^{\text{wag}}$	−0.186	−0.137	−0.153	−0.193	−0.193
$C_2D_4\,p^e$	3	112	75	15	8[f]

[a] J. L. Duncan, D. C. McKean, and P. D. Mallinson, *J. Mol. Spectrosc.*, **45**, 221 (1973). [b] Reference 37. [c] See footnote c, Table VII. [d] See Figure 1 for a description of the compliance constants. [e] See footnote i, Table I. [f] Owing to the high correlation between the potential constants two isotopic sets of frequencies were required for the A_{1g} block. p for the eight C_2D_4 frequencies not used in the MOCIC refinement is 10 cm^{-1}.

Table IX. SCF–MO Sources for MOCIC Constraints[a]

	H$_2$O[b,c]			BF$_3$		NH$_3$	
	MNDO	Ab initio		MNDO		MNDO	Ab initio
C_{11}	0.1075	0.1110	C_{33}	0.1010	C_{11}	0.1392	0.1430
C_{12}	−0.0471	−0.0556	C_{34}	0.0853	C_{12}	−0.0966	−0.1163
C_{22}	0.9478	1.2385	C_{44}	1.8967	C_{22}	1.1785	1.8217
					C_{33}	0.1445	0.1363
					C_{34}	0.0395	0.0338
					C_{44}	1.2387	1.3858

	NF$_3$			CH$_4$			CF$_4$	
	MNDO	Ab initio		MNDO	Ab initio		MNDO	
C_{11}	0.0702	0.0817	C_{33}	0.1743	0.1886	C_{33}	0.1067	
C_{12}	−0.0517	−0.0465	C_{34}	−0.1037	−0.0744	C_{34}	−0.1022	
C_{22}	0.5997	0.7658	C_{44}	1.9497	1.9825	C_{44}	1.1197	
C_{33}	0.1062	0.0969						
C_{34}	0.0587	0.0433						
C_{44}	0.9269	1.0902						

	CH$_3$F[d]			C$_2$H$_4$[e]	
	MNDO			MNDO	Ab initio
C_{11}	0.1605		C_{11}	0.1505	0.1685
C_{12}	−0.0303		C_{12}	−0.0115	−0.0041
C_{13}	−0.0154		C_{13}	−0.0448	−0.0255
C_{22}	1.7440		C_{22}	0.0875	0.1028
C_{23}	0.1020		C_{23}	0.0894	0.0662
C_{33}	0.0939		C_{33}	2.5275	2.0742
C_{44}	0.1836		C_{55}	0.1670	0.1729
C_{45}	0.0762		C_{56}	−0.1094	−0.0578
C_{46}	−0.0642		C_{66}	2.1088	1.6270
C_{55}	2.2427		C_{99}	0.1659	0.1699
C_{56}	0.2515		C_{910}	−0.1064	−0.0336
C_{66}	1.2432		C_{1010}	2.4182	2.2538
			C_{1111}	0.1504	0.1691
			C_{1112}	−0.0455	−0.0382
			C_{1212}	2.6225	2.2210

[a] The dimension is Å/mdyn. Methyl fluoride and ethylene are scaled with the C–H bond length. [b] The valence constraints are available upon request from B. I. Swanson. [c] The symmetry represented by C_{ij} is listed in K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1970. The unitary compliance matrices have been deleted. [d] The corresponding symmetry coordinates are in the reference of footnote a in Table VII. [e] The symmetry coordinates are discussed in the reference of footnote a in Table VIII. The unitary compliant matrices have been deleted.

The results presented here point to interesting aspects of both MNDO and ab initio methods. Both MO schemes often underestimate the primary stretch compliants. On the other hand, both approaches give reliable estimates of interaction coordinates, particularly symmetry interaction coordinates. The physical meaning is that MNDO and ab initio molecular orbital methods give reliable estimates of the initial part of a dissociation pathway since the interaction displacement coordinates are directly related to the MEP for unimolecular dissociation in the quadratic limit.[27] The fact that the molecular orbital schemes overestimate the relaxed force constant, the reciprocal of the primary compliant, indicates that they overestimate the restoring force for a distortion along this dissociation path.

References and Notes

(1) L. H. Jones and B. I. Swanson, *Acc. Chem. Res.*, **9**, 128 (1976).
(2) T. Shimanouchi in "Physical Chemistry, an Advanced Treatise", Vol. 4, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N.Y., 1970, Chapter 6.
(3) J. L. Duncan, *Spec. Period. Rep., Mol. Spectrosc.*, **3** (1976).
(4) L. H. Jones, R. S. McDowell, and B. I. Swanson, *J. Chem. Phys.*, **58**, 3757 (1973).
(5) J. L. Duncan, *Spectrochim. Acta*, **20**, 1197 (1965).
(6) A. Muller and B. Krebs, *J. Mol. Spectrosc.*, **24**, 180 (1967).
(7) T. Shimanouchi, I. Nakagawa, J. Hiraishi, and M. Ishi, *J. Mol. Spectrosc.*, **19**, 78 (1965).
(8) J. Tyson, H. H. Claassen, and H. Kim, *J. Chem. Phys.*, **54**, 3142 (1971).
(9) I. M. Mills, *Spectrochim. Acta*, **19**, 1583 (1963).
(10) F. A. Cotton and C. J. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).
(11) J. W. Linnett and P. J. Wheatley, *Trans. Faraday Soc.*, **45**, 33, 39 (1949).
(12) P. Pulay, "Modern Theoretical Chemistry", Vol II, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1976.
(13) J. E. Boggs and S. Skaarup, *J. Mol. Struct.*, **30**, 389 (1976).
(14) L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.*, **63**, 4750 (1975).
(15) (a) P. Pulay and F. Torok, *Mol. Phys.*, **25**, 1153 (1973); (b) K. Kozmutza and P. Pulay, *Theor. Chim. Acta*, **37**, 67 (1975).
(16) (a) C. E. Blom, P. J. Slingerland, and C. Altona, *Mol. Phys.*, **31**, 1359 (1976); (b) C. E. Blom and C. Altona, *ibid.*, **31**, 1377 (1976); (c) C. E. Blom, L. P. Otto, and C. Altona, *ibid.*, **32**, 1137 (1976); (d) C. E. Blom and C. Altona, *ibid.*, in press; submitted for publication; C. E. Blom, A. Oskam and C. Altona, submitted for publication.
(17) B. J. Rosenberg, W. C. Ermler, and I. Shavitt, *J. Chem. Phys.*, **65**, 4072 (1976).
(18) W. J. Taylor and K. J. Pitzer, *J. Res. Natl. Bur. Stand.*, **38**, 1 (1947).
(19) J. C. Decius, *J. Chem. Phys.*, **38**, 241 (1963).
(20) P. G. Maslou, *Dokl. Akad. Nauk SSSR*, **67**, 819 (1949).
(21) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1046 (1939).
(22) L. H. Jones, *Coord. Chem. Rev.*, 1, 351 (1966).
(23) L. H. Jones and R. R. Ryan, *J. Chem. Phys.*, **52**, 2003 (1970).
(24) (a) M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977). (b) M. J. S. Dewar and H. S. Rzepa, *ibid.*, following papers in this issue; M. J. S. Dewar and M. L. McKee, *ibid.*, **99**, 5231 (1977).
(25) An earlier SCF–MO treatment based on the INDO approximation (MINDO/3) has been shown[26] to give potential constants which satisfactorily reproduce vibrational frequencies. Preliminary tests suggest that MNDO is somewhat better in this respect.
(26(M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **99**, 1685 (1977).
(27) B. I. Swanson, *J. Am. Chem. Soc.*, **98**, 3067 (1976).
(28) B. I. Swanson, J. J. Rafalko, H. S. Rzepa, and M. J. S. Dewar, *J. Am. Chem. Soc.*, **99**, 7829 (1977).
(29) B. I. Swanson and R. S. Ottinger, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., No. 208.
(30) J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules, III", Technical Report No. 263-62, Shell Development Co., Emeryville, Calif.
(31) M. J. S. Dewar and Y. Yamaguchi, unpublished results.
(32) C. A. Allen, Jr., and P. C. Cross, "Molecular Vib Rotors", Wiley, New York, N.Y., 1963; E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York, N.Y., 1955.
(33) P. Pulay, *Mol. Phys.*, **21**, 329 (1971).
(34) P. Pulay and W. Meyer, *J. Chem. Phys.*, **57**, 3337 (1972).
(35) W. Meyer and P. Pulay, *J. Chem. Phys.*, **56**, 2109 (1972).
(36) W. Sawodny and P. Pulay, *J. Mol. Spectrosc.*, **51**, 135 (1974).
(37) P. Pulay and W. Meyer, *J. Mol. Spectrosc.*, **40**, 59 (1971).

Ground States of Molecules. 45. MNDO Results for Molecules Containing Beryllium

Michael J. S. Dewar* and Henry S. Rzepa

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. Received February 7, 1977

Abstract: Calculations of heats of formation, molecular geometries, ionization potentials, and dipole moments are reported for more than 50 compounds containing beryllium. The two most stable structural forms of beryllium borohydride were calculated to be of D_{3d} and D_{2d} symmetry. The calculated molecular vibration frequencies for the former agree very well with assignments reported by Nibler, and additional frequencies observed by Nibler in the gas phase correlate well with the D_{2d} form. The most stable form of dicyclopentadienylberyllium is calculated to have one pentahapto and one monohapto ring, which agrees with the crystal but not the gas phase structure. The doubly face bridging isomer had calculated D_{5d} symmetry, with the metal atom at the center, in disagreement with the reported electron diffraction structure, where the metal is displaced by 0.22 Å. Several interesting structural features are reported for as yet unknown compounds containing BeO or BeN_2 units replacing the isoelectronic C_2 or C_3. Singlet–triplet separations in BeO agree with those reported by Schaefer et al.

Introduction

Previous papers[1-4] of this series have reported the development of a new semiempirical MO method (MNDO) and its application to numerous compounds of the first and second period elements, H, B, N, C, O, and F. The results were in very satisfactory agreement with experiment and definitely superior to those given by earlier treatments, in particular MINDO/3.[5] In view of this success, extension of MNDO to other elements, in particular to metals, has become a matter of considerable interest. Here we report the first MNDO results for a metal, namely, beryllium.

One of the major obstacles encountered in developing treatments of this kind is the paucity of reliable experimental data needed for parametrization, in particular gas-phase heats of formation, and beryllium is typical in this respect. Indeed the situation here is especially bad because recognition of the