of acceptor orbital may be found in $P(CH_3)_3$ and PF_3 (Figure 3), but there are several important quantitative differences. First, the energy of 7e in PF_3 is lower than that in PH_3 or $P(CH_3)_3$ (Figure 1). This will enhance back-bonding to PF_3, when complexed to a metal, relative to PH_3 and $P(CH_3)_3$. Second, the nature of the lowest unoccupied e orbital changes. In PH_3, 3e is a hybrid of 36% 3p and 23% 3d on phosphorus, while the respective percentages are 14% and 10% for $P(CH_3)_3$ (7e) and 44% and 23% for PF_3 (7e). Contrary to conventional wisdom,[28] which ascribes the π-acceptor properties of PF_3 to empty phosphorus 3d orbitals, the π-acceptor orbital on phosphorus mostly consists of phosphorus 3p character. Mixing in 3p orbital character has the effect (Figure 3) of directing the empty π orbital in the direction of the lone pair (i.e., where a metal would bind). In PF_3 the acceptor orbital contains the maximum amount of phosphorus 3p character and is directed most effectively toward the region where a metal would bind.

This behavior can be viewed in the context of a crystal field[29] bonding model. The more highly electronegative the substituent attached to P to the more ionic the bond will be. Consequently, the substituent valence orbitals will dominate the occupied bonding orbitals and the antibonding levels will acquire more character of phosphorus valence 3p orbitals. Note the antibonding P–F character in the 7e orbital for PF_3 (Figure 3).

Acknowledgment. This work was supported in part by the National Science Foundation (CHE-8210514 and DMR-8214966). The work Z.B.-Y. was supported in part by a Chaim Weizmann Fellowship. We thank Professor Mark Ratner for helpful discussions.

Registry No. PH_3, 7803-51-2; $P(CH_3)_3$, 594-09-2; PF_3, 7783-55-3.

---

[28] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; John Wiley & Sons: New York, 1980; pp 87–89.

[29] Schnulle, G. W.; Parr, R. G *J. Am. Chem. Soc.* **1972**, *94*, 8974–8993.

Combination of Theoretical ab Initio and Experimental Information To Obtain Reliable Harmonic Force Constants. Scaled Quantum Mechanical (SQM) Force Fields for Glyoxal, Acrolein, Butadiene, Formaldehyde, and Ethylene

Péter Pulay,[1a] Géza Fogarasi,*[1b] Gábor Pongor,[1c] James E. Boggs,[1d] and Anna Vargha[1e]

Contribution from the Institute for General and Inorganic Chemistry, Eötvös L. University, Budapest 8, Pf. 323, Hungary 1445, and the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. Received January 13, 1983

Abstract: Fully optimized geometries, complete in- and out-of-plane force fields, and dipole moment derivatives have been calculated for the title compounds at the ab initio Hartree–Fock level using the 4-21 Gaussian basis set. The theoretical information is combined with experimental data by fitting the calculated force constants through a few parameters to the observed frequencies to obtain the final, scaled quantum mechanical (SQM) force fields. Recommendations for a standard procedure of this type are given. The SQM force fields give excellent reproduction of the fundamental frequencies and are considered as approaching the best accuracy which can be achieved in a harmonic treatment. The infrared intensities obtained at this level of theory are only qualitative estimates, but they are still useful for making assignments more reliable.

Introduction

Harmonic force fields of polyatomic molecules play an important role in several branches of molecular spectroscopy. Apart from their most straightforward application, the prediction and interpretation of vibrational frequencies, they are important in dealing with quantities which depend on the form of vibrations, like infrared and Raman intensities, or the vibrational structure in ultraviolet and photoelectron spectra, as well as vibrational averaging effects on molecular geometries and dipole moments. Also, a satisfactory harmonic analysis must obviously precede an anharmonic study. With the mounting interest in excited vibrational states, the importance of the latter is rapidly increasing.

The purely empirical deduction of force fields from spectral data for molecules of medium complexity has been rather unsuccessful. Highly simplified models, e.g., the Urey–Bradley force field,[2] usually give a correct qualitative picture but their accuracy is insufficient. If the number of parameters is increased, the fitting procedure often converges to an unphysical solution. This can only be counteracted by increasing the number of independent experimental observables, e.g., by recording the spectra of isotopomers, but the possibilities here are limited. Moreover, unless a completely general harmonic force field can be used, which is possible only for the smallest molecules, there is always an arbitrariness in the choice of the terms retained. As a case in point, a recent empirical force field for glyoxal,[3] which reproduces the fundamental frequencies of the parent molecule and its deutero derivatives quite precisely, is extremely improbable in the light of the present study. Another difficulty in empirical force field determination is the fact that the correct choice and assignment of the fundamentals is by no means evident in larger molecules and requires some prior knowledge of the force field.

As to the theoretical approach, with the development of gradient techniques[4,5] and rapid progress in computer facilities, the a priori

---

[1] (a) Eötvös L. University, Budapest; present address: Department of Chemistry, University of Arkansas, Fayetteville, AR 72701. (b) Eötvös L. University, Budapest; during part of this work on leave at the University of Texas at Austin. (c) Eötvös L. University, Budapest; (d) The University of Texas at Austin. (e) Eötvös L. University, Budapest; present address: Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences, Budaörsi ut 45, 1112 Budapest, Hungary.

[2] Urey, H. C.; Bradley, C. A. *Phys. Rev.* **1931**, *38*, 1969–1978. Shimanouchi, T. *Pure Appl. Chem.* **1963**, *7*, 131–145.

[3] Cossart-Magos, C. *Spectrochim. Acta, Part A* **1978**, *34*, 415–421.

[4] Pulay, P. *Mol. Phys.* **1969**, *17*, 197–204.

0002-7863/83/1505-7037$01.50/0

quantum mechanical calculation of force constants has become an economically feasible procedure for relatively large molecules (e.g., benzene,[6] naphthalene[7]) at a reasonably high level: ab initio Hartree–Fock calculations using double zeta basis sets. A survey of early studies already shows[5,8] that such calculations yield harmonic, and even anharmonic, force constants to a much better accuracy than originally expected. The diagonal harmonic terms in valence coordinates are obtained within the reasonable accuracy of typically 10–30%; more importantly, the deviations are very systematic in a qualitative sense, in that the errors occur consistently as an overestimation; for similar bonds in similar systems, this overestimation is also quantitatively systematic, i.e., well transferable. The off-diagonal terms are of comparable accuracy, and, considering that experimental values for these exhibit larger relative errors, the theoretical results are often competitive or superior to all but the most precise experimental data.

While this accuracy is reassuring, it is obviously not quite sufficient to enable a purely theoretical approach to be an adequate source of force field information for moderate-sized molecules. Improvements in the ab initio procedure by extending the basis set and introducing electron correlation are possible, but at present such an extension is economically feasible only for the smallest molecules. Therefore, for most molecules of chemical interest, the only realistic route seems to be to stay at the Hartree–Fock level and combine theoretical and experimental information. Based on the observation that the remaining errors are mainly systematic, it is an obvious idea to introduce a few empirical parameters as scale factors for the direct calculated force constants, and fit the parameters to the observed vibrational frequencies. If it is found, as the available experience indicates and as will be checked here on a series of molecules, that a good fit can be achieved using only a few parameters, this clearly proves that the theoretical force field is essentially correct, its residual errors are systematic, and the latter can be accounted for by scaling.

The possible usefulness of a combination of theory and experiment was already suggested in one of the earliest ab initio force field studies.[9] Slightly different versions of scaling have been used with success by Botschwina,[10] Blom and Altona,[11] and ourselves,[12,13] as discussed below in the Method section. The value of this approach was particularly demonstrated by the impressive series of calculations by Blom and Altona.[14] While the results of the various scaling schemes are essentially the same, exact comparisons cannot be made due to differences, even if minor, in the procedure. Thus, for systematic studies, decisions should be made on the exact form of scaling and also on some related questions. The main purpose of this paper is to give recommendations for a standardized procedure. The final results of this approach, which we may call Scaled Quantum Mechanical (SQM) force fields, probably represent the limit in accuracy that can be achieved within the harmonic approximation.

It seems worth mentioning that the same approach has been fairly successful even at the semiempirical level.[13,15] Specifically, in relation with the present work, our earlier study of butadiene, acrolein and glyoxal[15] has shown that the scaled CNDO/2 results give most signs and relative magnitudes of force constants correctly but they are too crude to provide a good quantitative reproduction of the frequencies; errors over 50 cm^{-1} after scaling have been encountered. This probably holds also for other semiempirical and even minimum-basis ab initio calculations. Nevertheless, these simpler theoretical models could be of considerable value in extrapolating the results obtained in studies of medium-sized molecules to larger systems. It should be mentioned that the reproduction of the frequencies by scaled CNDO/2 force fields can be markedly improved by introducing separate scale factors for the skeletal and the CH deformations. Nevertheless, as the results of a comprehensive study[16] show, the quantitative agreement is still much inferior as compared to the ab initio results.

We shall demonstrate the SQM method on a family of related compounds: the trans forms of glyoxal, acrolein, and butadiene, as well as formaldehyde and ethylene. Note that there are several ab initio calculations available for these molecules. Specifically, when our work was already in progress, Bock, George, and Trachtman[17] published several papers on the structure of *cis*- and *trans*-butadiene and on the structures and in-plane force constants of glyoxal and acrolein, using a $7s3p/3s$ basis set for glyoxal and butadiene, and a 4-31G set for acrolein. They also used a simple scaling procedure, with the scale factors transferred from simple molecules. Although the results are quite similar, our present calculations are superior in several points: ours is a very systematic approach which treats several molecules simultaneously, and our results are more complete as they include the out-of-plane force fields as well as the infrared intensities. In addition, the internal coordinate system used here conforms to our previous recommendations[8] and is preferable to the one used in ref 17.

Delocalized systems seem to be especially suited to demonstrate the method: the transferability of scale factors is of special importance in a family of molecules like these, where transferability can hardly be expected from the force constants themselves. On the basis of complete reliable force fields, we can also obtain important information on how far-reaching the interactions are in a conjugated chain. The latter is an important question if one realizes that beyond a certain size, force fields of larger molecules necessarily have to be built up of segments.

It is of interest to compare the present method with the empirical Consistent Force Field (CFF) technique.[18] The latter is very successful in predicting geometries for saturated hydrocarbons. In our opinion, however, its accuracy is not quite sufficient for vibrational spectroscopy. Moreover, the results are much less accurate for molecules containing heteroatoms. In its original form, the CFF method cannot be applied to conjugated systems where long-range interactions are important. For this reason, Warshel and Karplus[19] combined a semiempirical π-electron calculation with the CFF method to generate a potential surface for polyenes. This approach yields a resonable first guess to the potential function but illustrates the limitations of the method. There are occasional large deviations (e.g., the 911 cm^{-1} b_g band in *trans*-butadiene is calculated as 980 cm^{-1}; another b_g band is calculated at 680 cm^{-1} and fits thus the then accepted fundamental frequency of 679 cm^{-1}. However, this band has been since reassigned to 753 cm^{-1}, and our results make this reassignment conclusive; even larger deviations are encountered for benzene, e.g., 707 cm^{-1} observed, 615 cm^{-1} calculated; 1309 cm^{-1} observed, 1460 cm^{-1} calculated). In our opinion, the accuracy of the Warshel–Karplus method is insufficient to correct empirical misassignments.

Method

Our method for the systematic ab initio calculation of force constants has been described previously.[8] All the results presented

---

(5) Pulay, P. In "Modern Theoretical Chemistry"; Schaefer III, H. F., Ed.; Plenum: New York, 1977, Vo.. 4, pp 153–185.

(6) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999–4014.

(7) Sellers, H.; Pulay, P.; Boggs, J. E. to be published.

(8) Pulay, P.; Fogarasi, G.; Pang, F.; Boggs, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 2550–2560.

(9) Pulay, P.; Meyer, W. *J. Mol.* Spectrosc. **1971**, *40*, 59–70.

(10) (a) Botschwina, P. *Chem. Phys. Lett.* **1974**, *29*, 98–101. (b) *Ibid.* **1974**, *29*, 580–584.

(11) (a) Blom, C. E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377–1391. (b) Blom, C. E.; Slingerland, P. J.; Altona, C. *Ibid.* **1976**, *31*, 1359–1376.

(12) Fogarasi, G.; Pulay, P.; Molt, K.; Sawodny, W. *Mol. Phys.* **1977**, *33*, 1565–1570.

(13) (a) Török, F.; Hegedüs, A.; Kosa, K.; Pulay, P. *J. Mol. Struct.* **1976**, *32*, 93–99. (b) Fogarasi, G.; Pulay, P. *Ibid.* **1977**, *39*, 275–280.

(14) (a) Blom, C. E.; Otto, L. P.; Altona, C. *Mol. Phys.* **1976**, *32*, 1137–1149. (b) Blom, C. E.; Altona, C.; Oskam, A. *Ibid.* **1977**, *34*, 557–571.

(15) Panchenko, Yu. N.; Pulay, P.; Török, F. *J. Mol. Struct.* **1976**, *34*, 283–289.

(16) Vargha, A. Master's Thesis, Institute for General and Inorganic Chemistry, Eötvös L. University, Budapest, 1978 (in Hungarian).

(17) (a) Bock, C. W.; George, P.; Trachtman, M. *J. Mol. Spectrosc.* **1979**, *78*, 248–256. (b) *Ibid* **1979**, *78*, 298–308. (c) Bock, C. W.; George, P.; Mains, G. J.; Trachtman, M. *J. Mol. Struct.* **1978**, *49*, 211–214.

(18) (a) Lifson, S.; Warshel, A. *J. Chem.* Phys. **1968**, *49*, 5116–5129. (b) Warshel, A.; Lifson, S. *Ibid.* **1970**, *53*, 582–594.

(19) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5612–5625.

here are derived by the gradient (force) method,[4,5] using the program TEXAS.[20]

For systematic studies the following points are of primary importance: (1) the basis function set to be used in the quantum mechanical calculations; (2) selection of the reference geometry around which the force constants are evaluated; (3) a proper choice of vibrational internal coordinates; (4) selection of a well-defined and simple scaling procedure to fit the force constants to the experimental frequencies. Although the first three points have been discussed in detail earlier,[8] a brief summary with some additional remarks seems to be in order.

Our 4-21 Gaussian basis set[8] represents a reasonable compromise between sufficient completeness and economy. As compared to the 4-31G basis of Ditchfield et al.,[21] it gives very similar results for the potential surface which is the property of interest here, while saving nearly 50% of the computer time. The recently developed 3-21G basis set[22] is basically of equal quality to ours. It brings only insignificant improvement in economy, so that we see no reason to change to it, especially since a fairly large amount of calculations have been done with the 4-21 basis.

The choice of the reference geometry is the most difficult problem confronting the systematic ab initio calculation of force fields.[8] Because of anharmonicity, the theoretical force constants, particularly the stretching ones, depend significantly on the geometry adoped. For a single molecule, this can usually be absorbed in the scale factors, but for simultaneous calculations on several molecules a consistent way of determining reference geometries becomes mandatory. As discussed in ref 8, both experimental and uncorrected theoretical geometries have shortcomings, and the best procedure is to use empirically corrected theoretical geometries.[11] For hydrocarbons and oxo compounds the simple corrections established for the 4-21 basis set in ref 8 seem adequate. Note that only the bond lengths are corrected. A more comprehensive set of offset values for the 4-21 basis has been published by Schäfer et al.[23]

We would like to emphasize the importance of the choice of internal coordinates. A properly chosen coordinate set minimizes the coupling force constants and facilitates the transfer and comparison of force constants between related molecules. For this reason we advocate the use of *local* valence coordinates as specified in ref 8, except for ring systems.

Several scaling procedures have been used in the past. As suggested in ref 9, Botschwina[10] as well as our group in some early calculations[12] used the approach in which the coupling force constants are taken as calculated directly from the theory and only the diagonal terms are fitted to the experimental frequencies. In another procedure, as practiced by Blom and Altona,[11,14] the force constants are grouped according to the type of coordinate involved, a separate scale factor is introduced for each group, and the *complete* force field is scaled on the experimental frequencies. The coupling constants are put in one single group with a common factor. Both of these procedures have the slight disadvantage of being not invariant to certain coordinate transformations. For the latter, it also seems difficult to explain why quite different couplings should have the same factor.

The procedure advocated here was used first in our semiempirical calculations[13,15] and lately also in ab initio work.[6,7,24,25] It is invariant against linear transformations between coordinates that share the same scale factor. The coupling force constants are not independently scaled: if F_{ii} and F_{jj} are scaled by C_i and C_j, then $(C_iC_j)^{1/2}$ is used for F_{ij}. In matrix notation, we modify the theoretical force constant matrix, F^{th}, according to

$$F = C^{1/2}F^{th}C^{1/2}$$

where C is the diagonal matrix of scale factors. Coordinates which are similar in a chemical sense are scaled jointly, so that the number of independent parameters is usually much smaller than the dimension of F. In general, the number of variable scale factors should be determined as the minimum compatible with reasonable frequency reproduction.

The frequencies of isotope molecules, at least of those with well-estabished assignment, are usually included in the experimental data. It is also desirable to treat a family of related molecules simultaneously, using the same scale factor in all of the molecules for a specific type of coordinate. Due to the larger variety of bonds, this may lead to somewhat poorer reproduction of frequencies for an individual molecule but, obviously, the resulting optimized scale factors are of wider applicability for use in future work.

One may also consider the possibility of including additional data (Coriolis constants, etc.) in the fitting. Experience on simpler molecules, such as ethylene,[24] benzene,[6] and cyclobutane,[25] where such data are available, has shown that this is unnecessary. The frequencies alone fix the scale factors well enough so that if additional observables are calculated from the SQM force field afterwards, their reproduction is very satisfactory. In fact, one may note that, theoretically, the frequencies of one isotopomer (e.g., the parent molecule) should be sufficient for fixing the scaling. The inclusion of several isotopic molecules ensures, however, that random errors arising mainly from anharmonicity (and possible misassignments) are averaged out.

The values of scale factors are optimized by minimizing the weighted mean-square deviation between the calculated and the observed fundamental frequencies, using a program written by one of us (G.P.). In accordance with the suggestions above, the program is constructed to treat several isotopomers and/or a family of molecules simultaneously. The inverse vibrational frequencies are usually used as weights; this is a compromise between the assumption that the frequencies have the same absolute error (which requires equal weights) and that they have the same relative error (in this case, the weights should be proportional to ω^{-2}). Zero weights are assigned to missing or uncertain frequencies.

Obviously, it should be emphasized that none of the scaling procedures, including the one advocated here, has a strict theoretical basis. The differences are mainly in the different treatment of the diagonal and off-diagonal terms, respectively. The exact form of scaling the latter small terms is not a crucial point, however, if we accept, as experience proves, that their original (unscaled) ab initio values are essentially accurate (correct in sign and order of magnitude). The main effect of any scaling procedure is to scale down the diagonal force constants which are systematically overestimated at the Hartree–Fock level of quantum chemical calculations. Note that this assumption is not satisfied for a few molecules with cumulative multiple bonds, e.g., CO_2,[26] where coupling force constants are much more important than in general. Such molecules can be regarded as exceptions, however.

A final remark is necessary concerning the effects of anharmonicity. The harmonic approximation is an inevitable compromise for the treatment of larger molecules. The simple approach of using approximate harmonic corrections on the observed frequencies, as available, e.g., for ethylene,[27] is not used here because our aim is to predict the observed values. This means that systematic differences between effective and harmonic force constants are absorbed in our empirical scale factors. This is possible except in the case of CH/CD stretchings where the effective CD force constant should be greater than the effective

---

[20] Pulay, P. *Theor. Chim. Acta* **1979**, *50*, 599–312.

[21] Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem.* Phys. **1971**, *54*, 724–728.

[22] Binkley, J. S.; Pople, J. A. Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939–947.

[23] (a) Schäfer, L.; Van Alsenoy, C.; Scarsdale, J. N. *J. Chem. Phys.* **1982**, *76*, 1439–1444. (b) Klimkowski, V. J.; Ewbank, J. D.; Van Alsenoy, C.; Scarsdale, J. N.; Schäfer, L. *J. Am. Chem. Soc.* **1982**, *104*, 1476–1480.

[24] Fogarasi, G.; Pulay, P. *Acta Chim. Acad. Sci. Hung.* **1981**, *108*, 55–73.

[25] Bānhegyi, Gy.; Fogarasi, G.; Pulay, P. *J. Mol. Struct., THEOCHEM* **1982**, *89*, 1–13.

[26] Ha, T. K.; Blom, C. E.; Günthard, H. H. *Chem. Phys. Lett.* **1980**, *70*, 473–476. Note that we could not reproduce the deformational force constant given by these authors and believe that it is in error.

[27] Duncan, J. L.; McKean, D. C.; Mallinson, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221–246.

Table I. Definition of the Internal Coordinates[a]

in-plane	out-of-plane[b]
Glyoxal	
1. C–C st	1. C–C to = $1/2(\tau_{3124} + \tau_{5124} + \tau_{3126} + \tau_{5126})$
2. $C_1{=}O_3$ st	2. CH wa = H_5 out of 321 plane
3. $C_2{=}O_4$ st	3. CH wa′ = H_6 out of 412 plane
4. $C_1{-}H_5$ st	
5. $C_2{-}H_6$ st	
6. $C_2C_1O_3$ de = α_1	
7. $C_1C_2O_4$ de = α_2	
8. C_1H_5 ro = $2^{-1/2}(\beta_1-\beta_1')$	
9. C_2H_6 ro = $2^{-1/2}(\beta_2-\beta_2')$	
Acrolein	
1. C–C st	1. C–C to = $1/2(\tau_{3124} + \tau_{5124} + \tau_{3126} + \tau_{5126})$
2. $C_1{=}C_3$ st	2. CH^v wa = H_5 out of 321 plane
3. $C_2{=}O_4$ st	3. CH^f wa = H_6 out of 412 plane
4. $C_1{-}H_5$ st	4. CH_2 wa = C_1 out of 783 plane
5. $C_2{-}H_6$ st	5. CH_2 tw = $1/2(\tau_{7312} + \tau_{7315} + \tau_{8312} + \tau_{8315})$
6. $C_3{-}H_7$ st	
7. $C_3{-}H_8$ st	
8. CCC de = α_1	
9. CCO de = α_2	
10. C_1H_5 ro = $2^{-1/2}(\beta_1-\beta_1')$	
11. C_2H_6 ro = $2^{-1/2}(\beta_2-\beta_2')$	
12. CH_2 de = $6^{-1/2}(2\alpha_3-\beta_3-\beta_3')$	
13. CH_2 ro = $2^{-1/2}(\beta_3-\beta_3')$	
Formaldehyde	
1. C=O st	1. CH_2 wa = O out of 341 plane
2. $C{-}H_3$ st	
3. $C{-}H_4$ st	
4. CH_2 de = $6^{-1/2}(2\alpha-\beta-\beta')$	
5. CH_2 ro = $2^{-1/2}(\beta-\beta')$	
Butadiene	
1. C–C st	1. C–C to = $1/2(\tau_{3124} + \tau_{5124} + \tau_{3126} + \tau_{5126})$
2. $C_1{=}C_3$ st	2. CH wa = H_5 out of 321 plane
3. $C_2{=}C_4$ st	3. CH wa′ = H_6 out of 412 plane
4. $C_1{-}H_5$ st	4. CH_2 wa = C_1 out of 793 plane
5. $C_2{-}H_6$ st	5. CH_2 wa′ = C_2 out of 8,10,4 plane
6. $C_3{-}H_7$ st	6. CH_2 tw = $1/2(\tau_{7312} + \tau_{7315} + \tau_{9312} + \tau_{9315})$
7. $C_4{-}H_8$ st	7. CH_2 tw′ = $1/2(\tau_{8421} + \tau_{8426} + \tau_{10,4,2,1} + \tau_{10,4,2,6})$
8. $C_3{-}H_9$ st	
9. $C_4{-}H_{10}$ st	
10. CCC de = α_1	
11. CCC de′ = α_2	
12. CH^v ro = $2^{-1/2}(\beta_1-\beta_1')$	
13. CH^v ro′ = $2^{-1/2}(\beta_2-\beta_2')$	
14. CH_2 de = $6^{-1/2}(2\alpha_3-\beta_3-\beta_3')$	
15. CH_2 de′ = $6^{-1/2}(2\alpha_4-\beta_4-\beta_4')$	
16. CH_2 ro = $2^{-1/2}(\beta_3-\beta_3')$	
17. CH_2 ro′ = $2^{-1/2}(\beta_4-\beta_4')$	
Ethylene	
1. C=C st	1. CH_2 wa = C_2 out of 341 plane
2. $C_1{-}H_3$ st	2. CH_2 wa′ = C_1 out of 652 plane
3. $C_1{-}H_4$ st	3. CH_2 tw = $1/2(\tau_{3125} + \tau_{3126} + \tau_{4125} + \tau_{4126})$
4. $C_2{-}H_5$ st	
5. $C_2{-}H_6$ st	
6. CH_2 de = $6^{-1/2}(2\alpha_1-\beta_1-\beta_1')$	
7. CH_2 de′ = $6^{-1/2}(2\alpha_2-\beta_2-\beta_2')$	
8. CH_2 ro = $2^{-1/2}(\beta_1-\beta_1')$	
9. CH_2 ro′ = $2^{-1/2}(\beta_2-\beta_2')$	

[a] See Figure 1. [b] The sign of the torsional coordinates is defined according to: Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955; p 60. The signs of the out-of-plane coordinates are defined as follows: the coordinate value is positive if the atom brought out of the plane moves toward the reader in Figure 1.

CH one. This leads to a consistent overestimation of the CH stretching frequencies and underestimation of the CD ones, but is otherwise inconsequential. Anharmonicity has not only a systematic effect, like decreasing the frequency of the stretching vibrations relative to the harmonic values, but random ones too, caused mainly by Fermi resonances. These remain necessarily unaccounted for in a harmonic treatment. Their magnitude can reach ~20 cm^{-1}, and they probably contribute significantly to our residual errors.

Calculational Details

The complete harmonic general valence force fields of the trans forms of glyoxal, acrolein, and butadiene have been calculated in accordance with the recommendations given above. For completeness, formaldehyde and ethylene have also been included. The 4-21 Gaussian basis set[8] was used throughout. The system of internal coordinates is defined in Figure 1 and Table I.

Prior to the calculation of force constants, completely optimized geometries have been determined by the force relaxation method.[4,5] The reference geometries have been obtained from these by applying the systematic corrections to ref 8.

Our ab initio calculations yield also the dipole moment derivatives with respect to the internal coordinates, as the numerical difference of the dipole moment at the distorted geometries. These, in conjunction with the calculated normal coordinates, were used to estimate the infrared intensities.[28]

For the approximate characterization of a vibration we use the "*M* matrix",[29] $M_{ip} = L_{pi}(L^{-1})_{ip}$ where M_{ip} characterizes the participation of the *p*th internal coordinate in the *i*th normal mode. This method seems to have some advantage over the conventional potential energy distribution (PED) method, as all significant contributions have been found to be positive, and they add up to 1. The vibrational characters determined this way were found to correlate well with the spectroscopist's intuitive notion.

Results

Geometries. The theoretical geometries and the reference geometries obtained after the systematic corrections[8] are shown in Table II together with recent experimental values. In general, agreement between our reference geometries and the experimental values is good, the largest deviations appearing for hydrogen positions. This can be attributed partly to the large zero-point amplitude of the vibrations involving hydrogen atoms (note that our reference geometries are intended to approximate the experimentally generally unknown equilibrium structures), and partly to the inherently lower precision of the experimental H positions, particularly in electron diffraction. One noteworthy deviation occurs for the C–C bond length in glyoxal where our corrected theoretical reference geometry is about 0.02 Å shorter than the r_z value obtained by Kuchitsu et al.[30] from a careful combination of electron diffraction and rotational data (1.503 Å vs. 1.525 Å). This deviation, which is also shown by previous double-ζ calculations,[31] was already noticed by Bock et al.,[17c] who conclude tht

---

(28) Jalsovszky, Gy.; Pulay, P. *J. Mol. Struct.* **1975**, *26*, 277–287.

(29) (a) Pulay, P.; Török, F. *Acta Chim. Acad. Sci. Hung.* **1965**, *47*, 273–279. (b) Keresztury, G.; Jalsovszky, Gy. *J. Mol. Struct.* **1971**, *10*, 304–305.

(30) Kuchitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1968**, *1*, 463–479.

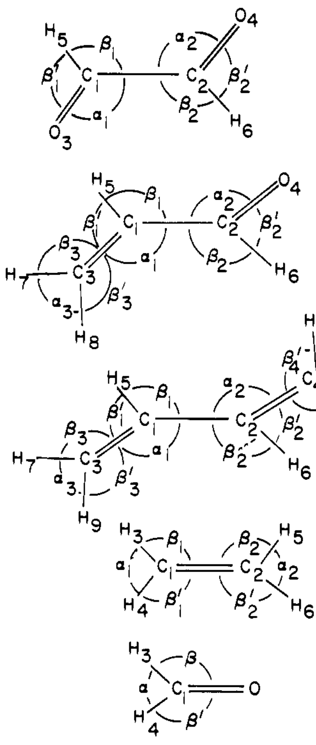

Figure 1. Numbering of the atoms and definition of primitive in-plane vibrational coordinates.

Kuchitsu's bond length is probably too long. However suggestive this conclusion is, it is based on the assumption that the quality of the wave function, and hence the error in the geometry, is similar for carbonyl and hydrocarbon compounds. This assumption is not true because polarization functions, mainly *d* functions on the carbon, are apparently much more important for the carbonyl group than e.g. for methylene[8]. For instance, the significant lengthening of the aldehydic CH bond relative to hydrocarbons can only be reproduced if polarization functions are used[8] (cf. our different correction value used for the aldehydic CH and the hydrocarbon CH). The need for a different correction value for the C–C bond in a CC=O group has been pointed out by Schäfer et al.[23]

To test the effect of polarization functions on the C–C bond length, we have repeated the geometry optimization of glyoxal using the 5-31G* basis set of the Pople group.[32] The following results were obtained: r(C–C) = 1.517 Å, r(C=O) = 1.184 Å, r(C–H) = 1.091 Å, α(CCO) = 121.1°, and α(OCH) = 123.6°. To account for the neglect of electron correlation, we have determined empirical correction (offset) values for these bond lengths from the corresponding geometries of ethane and formaldehyde:[8] these amount to −0.001, +0.019, and +0.007 Å, respectively. This leads to the following estimates for the equilibrium r_e bond lengths in glyoxal: r_e(C–C) = 1.516, r_e(C–O) = 1.203 and r_e(C–H) = 1.098 Å. Note that the C=O and C—H values agree with the corrected 4-21 data (see Table II), but the C–C value is significantly longer. The polarization function calculations thus confirm the values of Kuchitsu et al.,[30] which are, in this order, 1.525, 1.208, and 1.116 Å. The remaining differences are in the expected range of systematic deviations between an r_e and r_z structure.

Table II. Comparison of Theoretical, Reference, and Experimental Geometries[a]

parameter[b]	theoret r_e	ref[c] r_e	exptl[d] r_{av}	exptl[d] r_e
		Glyoxal		
CH	108.30	109.90	111.6 ± 8	
C–C	151.31	150.29	152.5 ± 3	
C=O	120.69	120.19	120.7 ± 2	
CCO ∠	120.88		121.2 ± 2	
HCO ∠	124.10		126.6 ± 2	
energy	−226.04001			
		Acrolein		
C_2H_6 (formyl)	108.88	110.48	112.3 ± 27	
C_1H_5 (vinyl α)	107.17	107.67	109.4 ± 10	
C_3H_7 (vinyl trans)	107.18	107.68		
C_3H_8 (vinyl cis)	107.49	107.99		
C–C	147.71	147.27	147.8 ± 5	
C=C	131.65	133.77	133.5 ± 5	
C=O	121.23	120.73	120.8 ± 5	
CCC	121.01		121.0 ± 7	
CCO ∠	124.05		124.0 ± 7	
β_2'(H–C=O) ∠	121.24		122.3 ± 27	
β_1'(H_5–C=C) ∠	122.52		120.7 ± 13	
β_3(H_7–C=C) ∠	122.26			
β_3'(H_8–C=C) ∠	121.64			
energy	−190.32716			
		Butadiene		
C_1H_5 (vinyl α)	107.54	108.04	109.0 ± 4	
C_3H_7 (vinyl trans)	107.20	107.70		
C_3H_9 (vinyl cis)	107.39	107.89		
C–C	147.03	146.70	146.3 ± 3	
C=C	131.86	133.96	134.1 ± 2	
CCC	123.98		123.3 ± 5	
β_1'(H_5–C=C)	119.99		121.8 ± 12	
β_3(H_7–C=C)	121.91			
β_3'(H_9–C=C)	121.84			
energy	−154.60068			
		Ethylene		
CH	107.3	107.8	109.0 ± 2	108.1
C=C	131.2	133.4	133.6 ± 2	133.4
HCC	122.0		121.4 ± 3	121.3
energy	−77.87080			
		Formaldehyde		
CH	108.4	110.0	111.6 ± 7	109.9
C=O	120.8	120.3	120.8 ± 3	120.3
HCO	122.4		122.8 ± 3	121.8
energy	−113.58872			

[a] Bond lengths in pm, angles in degrees, energies in $E_h \simeq$ 4.359814 aJ. [b] See Figure 1. [c] See text for the choice of the reference geometry. Values not shown are equal to the theoretical ones. [d] The average values have been taken from Kuchitsu et al.[30] The uncertainties shown refer to the last decimal written out. For butadiene see also Haugen, W.; Traetteberg, M. *Acta Chem. Scand.* 1966, *20*, 1726–1728. The equilibrium structures of ethylene and formaldehyde are taken from Duncan, J. L. *Mol. Phys.* 1974, *28*, 1177–1191, and Yamada, K.; Nakagawa, T.; Kuchitsu, K.; Morino, Y. *J. Mol. Spectrosc.* 1971, *38*, 70–83.

Table II shows that the calculated HCO angle in glyoxal is 2.5° smaller than the value quoted in ref 30. For an angle like this, theoretical estimates are usually much more accurate[8] (note that the theoretical angle calculated with the C–C bond length fixed at the value of ref 30 still deviates by more than 2° from the theoretical value). If we assume that the theoretical value is correct, then the C–C bond length of ref 30 must be revised downward; this would result in a slight decrease of the experimental r_z(C–C) distance.

It is interesting to note that in the series glyoxal, acrolein, and butadiene, the C—C=C and C—C=O bond angles vary rather erratically (Table II). This experimental finding[30] is fully confirmed by the calculations. The increase in the C–H (formyl) bond length on going from glyoxal to acrolein is also confirmed; it is probably due to the increase in the C—C=C angle, which according to the VSEPR model,[33] tends to increase the C–H distance.

---

(31) Dykstra, C. E.; Schaefer, H. F. *J. Am. Chem. Soc.* **1975**, *97*, 7210–7215.

(32) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(33) Gillespie, R. J. "Molecular Geometry"; Van Nostrand: London, 1972.

Table III. Optimized Scale Factors

scale factor	this work[a]	benzene[b]	recommended 4-21 value	Blom[c] 4-31G
CH stretching	0.8677 (11)	0.863	0.866	0.881-0.890
C=C stretching	0.8657 (46)	-	0.866	0.869, 0.872
C-C stretching	0.9215 (87)	0.919	0.920	0.887, 0.909
C=O stretching	0.8264 (30)	-	0.826	(C-O 0.856)
CCC,CCH in-plane def.	0.8025 (23)	0.794	0.800	0.793-0.816
C-C=O, CH formyl def.	0.8361 (31)	-	0.836	(H-C-O 0.85)
CH, CH_2 wagging	0.7217 (28)	0.739	0.730	0.718-0.746
CH formyl wagging	0.7867 (31)	-	0.787	-
C=C torsion	0.7837 (46)	0.768	0.776	0.793-0.816[d]

[a] The standard deviation (in parentheses) is included only to give a crude measure of the uncertainties in the scale factors. It has been assumed that the fundamental frequencies have a standard deviation of $(\nu \times 0.1\ cm^{-1})^{1/2}$, i.e., 5.5 cm^{-1} at 300 cm^{-1} and 17.3 cm^{-1} at 3000 cm^{-1}. This estimate includes both genuine experimental error, and, more importantly, errors in the harmonic treatment of the molecular vibrations. Note that the C-C torsional force constants have been formally also scaled. The following C-C torsion scale factors have been obtained for glyoxal, 0.398; for acrolein, 0.752; for butadiene, 1.095. The use of separate scale factors in each case is practically equivalent to determining the value of this force constant from the experimental spectrum, as a basis set not containing polarization functions cannot be expected to yield reliable values for this very shallow potential function. [b] Reference 6, Set I. [c] References 11 and 14. Note the difference in the scaling procedure. [d] Scaled together with the in-plane deformations.

Normal Frequencies and Related Quantities. Our final SQM force fields have been determined from the quantum-mechanical force fields by least-squares scaling to the observed fundamentals, as described in the Method section. The optimized scale factors are given in Table III, together with the values of Blom and Altona[11,14] and those obtained for benzene.[6] The observed and calculated frequencies are compared in Tables IV–VII. The SQM force fields are given in a compact form in Tables VIII and IX. For each molecule, only the light and the perdeuterated forms were included in the least-squares scale factor fitting procedure. This is reasonable as the fitting program cannot utilize frequency shifts directly, and the vibrational assignments of partially deutereated forms are in some instances uncertain. There are two exceptions to the above: both glyoxal-d_1 and -d_2 were included in the fitting procedure, and in acrolein CH_2CHCOD replaced the perdeutero form, as the gas-phase frequencies of the latter were not available. We have calculated many other deuterium frequencies and heavy-isotope shifts. For butadiene, they agree very well with the empirical assignment of Panchenko et al.[34] To conserve space, these values are not given as they can be easily calculated from the force fields of Tables VIII and IX.

The optimized scale factors agree very well with the corresponding values for benzene.[6] Interestingly, these factors agree well also with the figures of Blom and Altona,[11,14] in spite of the different basis set, scaling procedure and reference geometries, of which the last point is probably most important. For example, their systematically higher C–H stretching scale factors are due to the longer reference C–H bond used. This gives hope that our results can be combined with those of other groups employing the 4-31G basis set.

The standard deviation of the C–C stretching scale factor (see the notes to Table III) is larger than for the others, implying larger uncertainty. This is caused by the strongly mixed character of the C–C stretching vibrations, and also manifests itself in the relatively strong correlation between the C–C stretching and the

Table IV. Calculated and Observed Fundamental Vibrational Frequencies and Infrared Intensities of Glyoxal, Glyoxal-d_2, and Glyoxal-d_1

	glyoxal-h_2						glyoxal-d_2					glyoxal-d_1				
symm.	calcd[a]	obsd[b]	error, %[c]	int.[d]	ϑ[e]	char.[f]	calcd[a]	obsd[b]	error, %[c]	int.[d]	ϑ[e]	calcd[a]	obsd[b]	error, %[c]	int.[d]	ϑ[e]
								In-Plane								
a_g	2846	2844	0.1	0		CH st	2117	2138	−0.6	0		2846	2835	0.5	47.1	−71
bu	2846	2835	0.4	94.2	−71	CH st	2117	2130	−0.9	75.9	−91	2117	2130	−0.6	38.2	−92
a_g	1762	1745	1.0	0		CO st	1738	1722	0.9	0		1753	1735	1.0	15.8	22
b_u	1729	1732	−0.2	164.8	18	CO st	1700	1710	−0.6	157.3	11	1711	1717	−0.3	144.8	14
a_g	1344	1338	0.5	0		CH ro	924	932	−0.9	0		1333	1335	−0.1	9.0	−69
b_u	1321	1312	0.7	19.7	−70	CH ro	1014	1010	0.4	26.5	−65	967	972	−0.6	10.4	−63
a_g	1060	1065	−0.4	0		CC st, CCO de	1096	(1130)[g]	-	0		1081	(~1000)[h]	-	4.4	−69
a_g	563	551	2.1	0		CCO de, CC st	552	537	2.8	0		558	542	2.9	0.2	−63
b_u	326	339	−3.8	68.8	−62	CCO de	301	311	−3.2	56.9	−61	313	324	−3.5	62.0	−62
								Out-of-Plane								
b_g	1049	1048	0.1	0		CH wa	909	911	−0.2	0		998	999	−0.1	0.8	
a_u	789	801	−1.5	2.3		CH wa	623	630	−1.1	0.2		688	688	0.0	0.07	
a_u	(128)	127	-	47.4		CC to	117	118	−0.7	39.6		(123)	123	-	43.8	

[a] In cm^{-1}, rounded to the nearest integer. [b] The experimental frequencies adopted here have been compiled by Panchenko et al.[15] For light glyoxal, they agree to within ±3 cm^{-1} with those given by Harris.[40] [c] 100(calcd – obsd)/obsd. [d] Calculated infrared intensity in km/mol. [e] Angle of the transition dipole moment with the A main inertial axis, in degrees, given only for the in-plane infrared active fundamentals. The A/B hybrid ratio which determines the observed band contour is given by $\cos^2 \vartheta : \sin^2 \vartheta$. i.e. a pure A-type band corresponds to $\vartheta = 0$, a pure B-type to $\vartheta = \pm 90°$. Note that the predicted band contour for the C–C stretching fundamental in glyoxal-d_1 (calculated frequency 1081 cm^{-1}) is of type B, contrary to the speculation of Cole and Osborne.[39] [f] The dominant internal coordinates participating in the normal mode, obtained by the "M matrix" method[29] (see text). Abbreviations used: st, stretching; de, deformation; ro, rocking; wa, wagging; to, torsion; sc, scissoring; tw, twisting. To conserve space, the vibrational character is given only for the parent compound. The fundamental frequencies of the isotope substituted derivatives have been ordered to correspond approximately to the vibrational character given. [g] Deduced from combination bands.[39] [h] Frequency uncertain.[39]

---

(34) (a) Panchenko, Yu. N.; Pentin, Yu. A.; Tyulin, V. I.; Tatevskii, V. M. *Opt. Spektrosk.* **1964**, *16*, 992–997. (b) Benedetti, E.; Aglietto, M.; Pucci, S.; Panchenko, Yu. N.; Pentin, Yu. A.; Nikitin, O. T. *J. Mol. Struct.* **1978**, *49*, 293–299.

Table V. Calculated and Observed Fundamental Vibrational Frequencies and Infrared Intensities of Acrolein and Acrolein-d_1 (CH_2=CH–CDO)[a]

acrolein-h_4					acrolein-d_1			
calcd	obsd[b]	error, %	int.	char.[d]	calcd	obsd[b]	error, %	int.
				In-Plane				
3115	3102	0.4	8.0	CH_2 a-st	3115	3101	0.5	7.6
3082	(3000)	-	0.6	CH^v st	3082	(2988)	-	0.5
3024	3000	0.8	5.7	CH_2 s-st	3024	2988	1.2	5.6
2768	2777[c]	−0.3	88.9	CH^f st	2049	2060	−0.5	67.1
1732	1723	0.5	226.2	CO st	1713	1709	0.2	235.6
1623	1625	−0.1	0.2	C=C st, CH_2 sc	1622	1621	−0.1	0.1
1434	1422	0.9	5.4	CH_2 sc, CH^f ro	1419	1403	1.2	4.8
1383	1361	1.6	4.6	CH^f ro, CH_2 sc	1057	1060	−0.2	2.1
1266	1276	−0.8	0.7	CH^v ro, CH_2 sc	1266	1275	−0.7	0.6
1149	1159	−0.9	44.4	C–C st, CH^v ro, CH_2 ro	1145	1153	−0.7	39.7
910	913	0.3	23.5	CH_2 ro, C–C st	877	877	0.0	17.4
559	564	−0.8	10.6	CCO de, C–C st, CCC de	557	561	−0.8	10.5
314	324	−3.0	11.9	CCC de, CCO de	306	313	−2.4	11.3
				Out-of-Plane				
1003	993	1.1	7.0	CH_2 tw, CH^v wa	1003	993	1.0	5.0
1002	(980)[e]	-	0.04	CH^f wa	869	846	2.7	13.8
969	959	1.1	67.0	CH_2 wa	975	959	1.7	60.9
580	589	−1.5	16.4	CH^v wa, CH_2 tw	546	556	−1.8	10.6
(158)	158	-	7.1	C–C to	(151)	151	-	6.6

[a] See notes to Table IV. [b] The experimental frequencies were taken from the compilation of ref 15, except the 2777-cm^{-1} band, see footnote *c*. [c] Arithmetic mean of the Fermi doublet frequencies 2800 and 2754 cm^{-1}.[40] [d] Abbreviations used: CH^f, formyl CH; CH^v vinyl CH; s-st, symmetric stretching; a-st, antisymmetric stretching. See also Table IV. [e] Value deduced from the product rule by Brand, J. C. D.; Williamson, D. G. *Discuss. Faraday Soc.* 1963, *35*, 184–191.

Table VI. Calculated and Observed Fundamental Vibrational Frequencies and Infrared Intensities of Butadiene and Butadiene-d_6[a]

	butadiene-h_6					butadiene-d_6			
	calcd	obsd[b]	error, %	int.	char.	calcd	obsd[b]	error, %	int.
					In-Plane				
b_u	3112	3102	0.3	38.4	CH_2 a-st	2316	2355	−1.7	18.8
a_g	3111	3101	0.3	0	CH_2 a-st	2316	2341	−1.1	0
b_u	3045	3056	−0.4	13.2	CH^v st	1159	2255	0.1	6.5
a_g	3042	3014	0.9	0	CH^v st	2258	2262	−0.2	0
b_u	3032	(2985)	–	14.8	CH_2 s-st	2210	2215	−0.2	7.4
a_g	3026	3014	0.6	0	CH_2 s-st	2208	2205	0.2	0
a_g	1665	1643	1.4	0	C=C, C–C st	1602	1583	1.2	0
b_u	1596	1599	−0.2	9.2	C=C st, CH_2 sc	1509	1523	−0.9	7.2
a_g	1458	1442	1.1	0	CH_2 sc	1044	1048	−0.4	0
b_u	1398	1385	0.9	1.0	CH_2 sc, C=C st	1056	1042	1.3	0.2
b_u	1302	1296	0.5	3.2	CH^v ro	1001	1009	−0.8	5.3
a_g	1289	1291	−0.2	0	CH^v ro, C=C st	927	919	0.9	0
a_g	1215	1205	0.9	0	mixed: C–C st, CH_2 ro	1180	1186	−0.5	0
b_u	999	991	0.8	2.7	CH_2 ro	749	739	1.4	1.6
a_g	882	890	−0.9	0	C–C st, CH_2 ro	736	741	−0.7	0
a_g	502	513	−2.2	0	CCC de	434	440	−1.4	0
b_u	287	301	−4.8	2.7	CCC de	241	240	−3.6	1.8
					Out-of-Plane				
a_u	1017	1013	0.4	32.2	CH_2 tw, CH wa	765	770	−0.7	0.3
b_g	968	967	0.1	0	CH wa, CH_2 tw	796	795	0.2	0
a_u	913	908	0.5	108.0	CH_2 wa	717	718	−0.2	79.1
b_g	913	911	0.2	0	CH_2 wa	691	702	−1.6	0
b_g	749	753	−0.6	0	CH_2 tw, CH wa	600	603	−0.5	0
a_u	516	524	−1.5	12.8	CH wa, CH_2 tw	376	381	−1.4	7.6
a_u	(163)	163	–	0.4	C–C to	(140)	140	–	0.3

[a] See notes to Tables IV and V. [b] The experimental frequencies have been taken from Panchenko et al.[15] except for the reversal in the assignment of the 770 and 741 cm^{-1} infrared-active fundamentals of butadiene-d_6.

in-plane deformational scale factors. The inclusion of a scale factor for C–C stretching, separate from C=C, may thus be questioned, as the average standard deviation of the frequencies decreases only marginally by this. Our motivation for separate scaling was that factors obtained this way are more compatible with those obtained for similar molecules.[6,11,14]

Both the present results and those of Blom et al.[11,14] show that the scale factors for C—C=O, H—C=O, and H—C—O deformations and waggings should be higher (closer to 1) than those for the corresponding C—C=C, H—C=C, H—C—C units. This is probably due to the electron withdrawal from the carbon by the neighboring oxygen which diminishes the effect of electron correlation on the carbon atom.

The fit of the frequencies, as shown by Tables IV–VII, is very good, the total root-mean-square error being only 12.3 cm^{-1} for the in-plane modes and 6.7 cm^{-1} for the out-of-plane mode. Perhaps even more significant is the fact that the individual deviations between the observed and calculated wave numbers are less than 20 cm^{-1}, except a few cases to be discussed below. The largest discrepancy occurs for the C–C stretching frequency of glyoxal-d_1 and glyoxal-d_2, particularly for the latter, where the discrepancy reaches 35 cm^{-1}. However, there is considerable experimental difficulty in observing the Raman spectrum of glyoxal[35-38] and the vapor-phase Raman spectrum could not be

Table VII. Calculated and Observed Fundamental Vibrational Frequencies and Infrared Intensities of Ethylene, Ethylene-d_4, Formaldehyde, and Formaldehyde-d_2[a]

	ethylene					ethylene-d_4			
	calcd	obsd[b]	error, %	int.	char.	calcd	obsd[b]	error, %	int.
					In-Plane				
b_{2u}	3120	3105	0.5	31.7	CH_2 a-st	2321	2345	−1.0	17.3
b_{1g}	3092	3086	0.2	0	CH_2 a-st	2303	2310	−0.3	0
a_g	3042	3026	0.5	0	CH_2 s-st	2255	2260	−0.2	0
b_{3u}	3022	3021	0.0	15.0	CH_2 s-st	2184	2200	−0.7	7.1
a_g	1626	1630	−0.2	0	C=C st, CH_2 sc	1500	1518	−1.2	0
b_{3u}	1455	1444	0.7	5.1	CH_2 sc	1078	1077	−0.1	3.0
a_g	1345	1342	0.2	0	CH_2 sc, C=C st	985	985	0.0	0
b_{1g}	1222	1220	0.2	0	CH_2 ro	996	1011	−1.5	0
b_{2u}	821	826	−0.6	0.7	CH_2 ro	590	(584)	-	0.4
					Out-of-Plane				
a_u	1025	1023	0.2	0	CH_2 tw	725	726	−0.1	0
b_{2g}	951	940	1.2	0	CH_2 wa	787	780	0.9	0
b_{1u}	933	949	−1.7	102.2	CH_2 wa	706	720	−2.1	58.5
	formaldehyde					formaldehyde-d_2			
					In-Plane				
b_2	2851	2843	0.3	118.8	CH_2 a-st	2125	2160	−1.6	86.1
a_1	2770	2782	−0.5	20.2	CH_2 s-st	2035	2056	−1.0	43.2
a_1	1734	1746	−0.7	82.3	C=O st	1667	1700	−2.0	65.9
a_1	1514	1500	0.9	11.7	CH_2 sc	1108	1106	0.2	1.1
b_2	1248	1249	−0.1	22.2	CH_2 ro	987	990	−0.3	21.0
					Out-of-Plane				
b_1	1166	1167	−0.1	3.9	CH_2 wa	936	938	−0.2	0.13

[a] See the notes to Tables IV to VI. [b] The experimental frequencies have been taken from ref 27 with the modification of Duncan, J. L.; Hegelund, F.; Foster, R. B.; Hills, G. W.; Jones, W. J. *J. Mol. Spectrosc.* 1976, *61*, 470–473, and from Duncan, J. L.; Mallinson, P. D. *Chem. Phys. Lett.* 1973, *23*, 597–599.

measured. The frequency values have been deduced from combination bands[39,40] and from condensed-phase spectra.[36-38] In fact, the frequency assignment of Cole and Osborne[39] does not satisfy the product rule in the A_{1g} species, not even after harmonic corrections have been applied to the C–H and C–D stretchings. A strong Fermi resonance with $2\nu_5$ is also apparent;[38] this may have shifted the ~1100-cm^{-1} frequency downward for glyoxal and upward for glyoxal-d_2. For acrolein, a missing CH stretching frequency has been assigned to 3000 cm^{-1} by Harris.[40] The present results show that the band in question should be hidden in the ~3100-cm^{-1} complex. There is little hope for its direct observation in that congested region, as the predicted infrared intensity is very small (Table V), due to a fortuitous cancellation of the transition dipole moments. This vibration is essentially the vinyl α CH stretching, with some admixture of the methylene antisymmetric CH stretching. There is a similar problem in the CH stretching region of butadiene, where the assignment of the Raman and infrared active CH_2 stretchings to 2985 and 3014 cm^{-1} by Harris[40] cannot be correct. Such a large splitting is excluded by the separation of the methylene groups, and indeed our calculations predict that the two frequencies are separated by only 2 cm^{-1}, in the reverse direction.

Note further that our results apparently exclude the possibility that the weak featureless band at about 732 cm^{-1}, observed by Harris[40] in the infrared spectrum of acrolein, is a fundamental. The "missing" out-of-plane vibration in acrolein should have a frequency near 1000 cm^{-1}. It has a very low predicted intensity, which accounts for the fact that it could not be observed.

Infrared Intensities. The calculated dipole moment derivatives have been used to evaluate the theoretical infrared intensities which are included in Tables IV–VII. No experimental values are given, as no accurate measurements seem to have been carried out for butadiene, acrolein, and glyoxal. For ethylene and formaldehyde, the present theoretical values are in reasonable agreement with the results of an earlier theoretical study which also gives improved experimental values.[28] More detailed results on ethylene, using also the 6-31G** polarization basis set, can be found in ref 24.

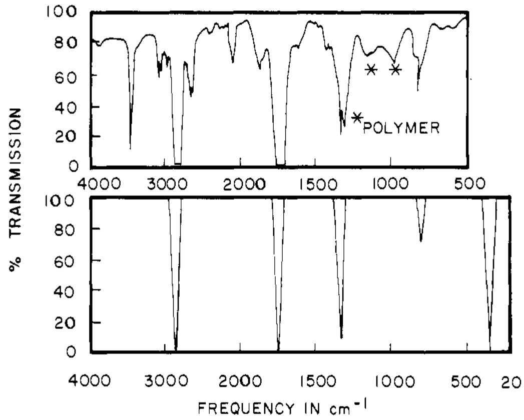

Figure 2. Comparison of the observed and calculated infrared spectrum of glyoxal. The experimental spectrum has been adopted from Harris (ref 40); both spectra correspond to 10 cm cell length and 235 torr pressure. The bands denoted by an asterisk are due to polymerization. The peak heights in the simulated spectra were evaluated by assuming a triangular band shape, 100 cm^{-1} wide at the base.

Previous experience[6,8,24,28] has shown that the prediction of intensities by double-ζ sp basis sets is only qualitative. Nevertheless, the present results may be useful in the identification and assignment of fundamentals. For example, all infrared active bands which had to be excluded from the fitting procedure because of missing or uncertain experimental data were found to be either very weak (intensity less than 1 km/mol) or weak (intensity less than 5 km/mol) and be close to a strong band. We compare in Figures 2–4 gas phase infrared spectra of glyoxal, acrolein, and butadiene with simulated spectra, based on the theoretical wavenumbers and intensities.

---

(35) Holzer, W.; Ramsay, D. A. *Can. J. Phys.* **1970**, *48*, 1759–1765.

(36) Verderame, F. D.; Castellucci, E.; Califano, S. *J. Chem. Phys.* **1970**, *52*, 719–723.

(37) Kho, L. K.; Tyulin, V. I. *Opt. Spektrosk.* **1973**, *35*, 770–772.

(38) Cole, A. R. H.; Durig, J. R. *J. Raman Spectrosc.* **1975**, *4*, 31–39.

(39) Cole, A. R. H.; Osborne, G. A. *Spectrochim. Acta, Part A* **1971**, *27*, 2461–2490.

(40) Harris, R. K. *Spectrochim. Acta* **1964**, *20*, 1129–1141.

Table VIII. Scaled Quantum Mechanical (SQM) In-Plane Force Constants[a]

Glyoxal

1 C–C st	*3.973*								
2 C=O st	*0.563*	*12.468*							
3 C=O st′	0.563	0.037	12.468						
4 C–H st	0.018	*0.330*	0.087	*4.453*					
5 C–H st′	0.018	0.087	0.330	0.015	4.453				
6 CCO de	*0.162*	*0.328*	*0.135*	−0.145	−0.027	1.203			
7 CCO de′	0.162	0.135	0.328	−0.027	−0.145	*0.333*	1.203		
8 CH ro	*0.156*	*−0.310*	−0.004	0.041	0.018	*0.122*	*−0.114*	*0.559*	
9 CH ro′	0.156	−0.004	−0.310	0.018	0.041	−0.114	0.122	*0.041*	0.559

Acrolein

1 C–C st	*4.726*												
2 C=C st	*0.307*	*8.731*											
3 C=O st	*0.695*	*−0.106*	*12.003*										
4 CH^{v} st	0.016	0.062	0.035	*5.220*									
5 CH^{f} st	0.081	0.040	*0.420*	0.005	*4.230*								
6 CH^{c} st	−0.006	0.049	0.008	0.015	0.000	5.221							
7 CH^{t} st	−0.007	0.083	0.006	−0.004	0.013	0.019	5.125						
8 CCC de	*0.263*	*0.213*	0.052	*−0.144*	−0.020	0.034	−0.052	*1.018*					
9 CCO de	*0.175*	0.087	*0.293*	−0.056	*−0.169*	0.015	−0.003	*0.217*	1.294				
10 CH^{v} ro	*0.145*	*−0.177*	−0.006	0.015	0.023	0.008	−0.022	0.027	*−0.098*	*0.470*			
11 CH^{f} ro	*0.204*	−0.011	*−0.328*	0.018	0.029	−0.004	0.012	−0.035	*0.083*	*0.036*	*0.643*		
12 CH$_2$ de	−0.005	*−0.204*	−0.003	−0.004	−0.010	0.056	0.051	−0.021	−0.019	0.015	−0.003	*0.453*	
13 CH$_2$ ro	0.027	0.010	0.033	−0.025	−0.004	0.101	−0.117	*0.074*	0.016	*0.037*	−0.002	−0.008	*0.523*

Butadiene

1 C–C st	*5.092*																
2 C=C st	*0.348*	*8.733*															
3 C=C st′	0.348	*−0.08*	8.733														
4 CH^{v} st	0.057	0.069	0.021	5.080													
5 CH^{v} st′	0.057	0.021	0.069	−0.001	5.080												
6 CH^{c} st	−0.004	0.058	0.007	0.015	−0.002	5.213											
7 CH^{c} st′	−0.004	0.007	0.058	−0.002	0.015	0.002	5.213										
8 CH^{t} st	0.007	0.069	−0.003	−0.001	0.012	0.028	0.001	5.157									
9 CH^{t} st′	0.007	−0.003	0.069	0.012	−0.001	0.001	0.028	−0.001	5.157								
10 CCC de	*0.211*	*0.197*	0.067	−0.160	−0.045	0.046	0.012	−0.053	−0.003	*1.037*							
11 CCC de′	0.211	0.067	0.197	−0.045	−0.160	0.012	0.046	−0.003	−0.053	*0.154*	1.037						
12 CH^{v} ro	*0.189*	*−0.190*	−0.012	−0.002	0.020	0.008	−0.004	−0.026	0.011	0.001	−0.047	*0.526*					
13 CH^{v} ro′	0.189	−0.012	−0.190	0.020	−0.002	−0.004	0.008	0.011	−0.026	−0.047	0.001	*0.038*	0.526				
14 CH$_2$ de	−0.008	*−0.216*	−0.003	−0.008	−0.007	0.056	−0.002	0.055	0.001	−0.016	−0.010	0.015	−0.003	*0.451*			
15 CH$_2$ de′	−0.008	−0.003	−0.216	−0.007	−0.008	−0.002	0.056	0.001	0.055	−0.010	−0.016	−0.003	0.015	0.000	0.451		
16 CH$_2$ ro	*0.042*	0.016	0.009	−0.031	−0.004	0.109	0.002	−0.111	0.003	*0.087*	0.013	*0.039*	−0.001	−0.006	−0.002	*0.534*	
17 CH$_2$ ro′	0.042	0.009	0.016	−0.004	−0.031	0.002	0.109	0.003	−0.111	0.013	0.087	−0.001	0.039	−0.002	−0.006	0.004	0.534

Ethylene

1 C=C st	*8.952*								
2 C–H st$_1$	0.075	*5.177*							
3 C–H st$_2$	0.075	0.027	5.177						
4 C–H st$_3$	0.075	0.015	−0.005	5.177					
5 C–H st$_4$	0.075	−0.005	0.015	0.027	5.177				
6 CH$_2$ de	*−0.212*	0.062	0.062	−0.009	−0.009	*0.455*			
7 CH$_2$ de′	−0.212	−0.009	−0.009	0.062	0.062	0.017	0.455		
8 CH$_2$ ro	0	−0.107	0.107	−0.036	0.036	0	0	*0.529*	
9 CH$_2$ ro′	0	−0.036	0.036	0.107	−0.107	0	0	*−0.081*	0.529

Formaldehyde

1 C=O st	*12.285*				
2 C–H st	*0.418*	*4.365*			
3 C–H st′	0.418	0.027	4.365		
4 CH$_2$ de	*−0.350*	0.069	0.069	*0.542*	
5 CH$_2$ ro	0	0.106	−0.106	0	*0.788*

---

[a] The units of force constants are compatible with the energy measured in aJ, bond lengths in Å = 100 pm, and bond angles in radians. Some noticeable force constants are italicized. See Table I for the definition of coordinates.

Table **IX**. Scaled Quantum Mechanical (SQM) Out-of-Plane Force Constants[a]

			Glyoxal				
1. C–C to	0.0126						
2. C–H wa	−0.0013	0.3479					
3. C–H wa′	−0.0013	−0.0435	0.3479				
			Acrolein				
1. C–C to	0.0251						
2. C–H^v wa	−0.0097	0.2397					
3. C–H^f wa	−0.0009	−0.0200	0.3727				
4. CH_2 wa	−0.0030	0.0244	−0.0075	0.2678			
5. CH_2 tw	0.0084	0.0005	0.0214	0.0011	0.1246		
			Formaldehyde				
1. CH_2 wa	0.3997						
			Butadiene				
1. C–C to	0.0309						
2. CH wa	−0.0054	0.2532					
3. CH wa′	−0.0054	−0.0150	0.2532				
4. CH_2 wa	−0.0003	0.0287	−0.0048	0.2377			
5. CH_2 wa′	−0.0003	−0.0048	0.0287	−0.0016	0.2377		
6. CH_2 tw	0.0057	−0.0029	0.0158	0.0002	0.0053	0.1245	
7. CH_2 tw′	0.0057	0.0158	−0.0029	0.0053	0.0002	−0.0060	0.1245
			Ethylene				
1. CH_2 wa	0.2573						
2. CH_2 wa′	0.0336	0.2573					
3. CH_2 tw	0	0	0.1304				

[a] For units, see Table VIII. The internal coordinates are defined in Table I.

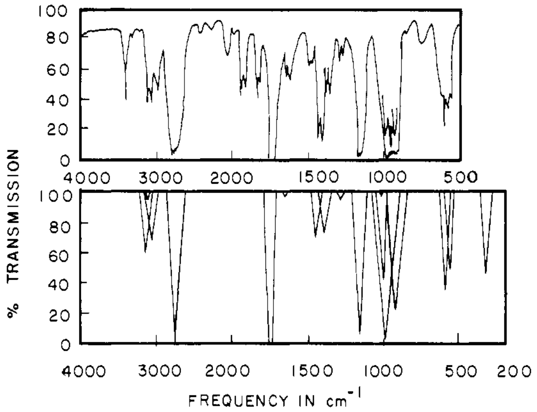

Figure 3. Comparison of the observed and calculated infrared spectrum of acrolein. The experimental spectrum has been adopted from Harris (ref 40); both spectra correspond to 10 cm cell length and 120 torr pressure (the second trace in the experimental spectrum was recorded at 50 torr). See Figure 2 for details of the simulation.

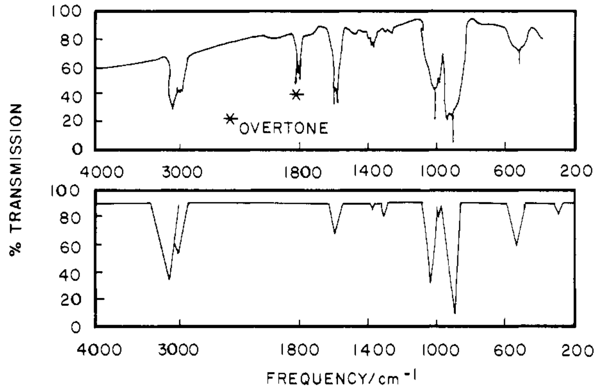

Figure 4. Comparison of the observed and calculated infrared spectrum of butadiene. The experimental spectrum was taken from the Sadtler Research Laboratories collection. The simulated spectrum corresponds to 50 torr pressure in a 10-cm cell. The pressure and path length used in recording the experimental spectrum are not known but are thought to be near these values. See also Figure 2.

The comparison of the theoretical and experimental spectra shows a reasonable agreement, indicating that even such relatively low-level calculations can greatly facilitate the assignment of fundamentals. Quantitative agreement, however, seems to require at least a double-ζ plus polarization-type basis set, and possibly also the inclusion of electron correlation.

Comparison with Experimental Force Fields. For the simplest molecules in the series, ethylene and formaldehyde, the agreement with the best experimental force fields[41,42] is very good. It is particularly pleasing that the newest General Valence Force Field for ethylene[42] is in substantially better agreement with the present and previous[9,24,43] ab initio force field than an earlier GVFF by the same author.[41] Comparison with results obtained using larger basis sets[24,44] suggests that the improvements obtained by extending the basis set are small and can be largely absorbed in the scale factors. Indeed, the scaled 4-21 and 6-31G** force fields for ethylene are virtually indistinguishable.[24]

For the other three molecules, there are no experimental GVFF's comparable in quality to the force fields of ethylene and formaldehyde. Of the three molecules, glyoxal is the simplest and the only one for which recent experimental force fields have been determined, so we shall limit our treatment to this molecule. Fukuyama et al.[45] have determined a Urey–Bradley force field for the in-plane vibrations, and a valence force field for the out-of-plane vibrations of glyoxal. Recently, Cossart-Magos[3] has published an in-plane valence force field. A comparison (not shown) of our values in Table VIII with those of Fukuyama et al.[45] shows the expected rather crude but qualitatively correct behavior of the Urey–Bradley model. On the other hand, the in-plane force field of Cossard–Magos[3] is qualitatively incorrect, in spite of the satisfactory reproduction of the normal frequencies of glyoxal and its deutero analogues. Table X shows a comparison of the two force fields in our coordinates. The force constants

---

(41) (a) Duncan, J. L.; McKean, D. C.; Mallinson, P. D. *J. Mol. Spectrosc.* **1973**, *45*, 221–246. (b) Duncan, J. L.; Mallinson, P. D. *Chem. Phys. Lett.* **1973**, *23*, 597–599.

(42) Duncan, J. L.; Hamilton, E. *J. Mol. Struct., THEOCHEM* **1981**, *76*, 65–80.

(43) Blom, C. E.; Altona, C. *Mol. Phys.* **1977**, *34*, 177–192.

(44) (a) Meyer, W.; Pulay, P. *Theor. Chim. Acta* **1974**, *32*, 253–264. (b) Jaquet, R.; Kutzelnigg, W.; Staemmler, V. *Theor. Chim. Acta* **1980**, *54*, 205–227.

(45) Fukuyama, T.; Kuchitsu, K.; Morino, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 3019–3020.

Table X. Comparison of the Experimental Force Field of Cossart-Magos[3] and the SQM Force Field of Glyoxal

diagonal terms	ref 3	this work
C–C st	4.700	3.973
C=O st	12.663	12.468
C–H st	4.396	4.453
CCO de	*0.827*	*1.203*
CH ro	0.548	0.559
coupling terms	**ref 3**	**this work**
C–C st, C=O st	0	0.563
C–C st, C–H st	0	0.018
C–C st, CCO de	*−0.151*	*+0.162*
C–C st, CH ro	0.884	0.156
C=O st, C=O st′	0.377	0.037
C=O st, C–H st	0.194	0.330
C=O st, C–H st′	0	0.087
C=O st, CCO de	0.269	0.328
C=O st, CCO de′	0	0.135
C=O st, CH ro	−0.134	−0.310
C=O st, CH ro′	0	−0.004
C–H st, C–H st′	0	0.015
C–H st, CCO de	0	−0.145
C–H st, CCO de′	0	−0.027
C–H st, C–H ro	0	0.041
C–H st, C–H ro′	0	0.018
CCO de, CCO de′	*−0.159*	*+0.333*
CCO de, CH ro	*0.576*	*0.122*
CCO de, CH ro′	*0.301*	*−0.114*
CH ro, CH ro′	0.024	0.041

[a] See Table VIII for units and the definition of coordinates. The most offending terms are italicized. All of these are associated with the CCO deformational and the CH rocking coordinate, suggesting that the force field fitting of ref 3 converged to an alternative, unphysical solution.

involving the CCO deformations and the CH rocking coordinate are in total disagreement with our values. Many of the coupling constants are unreasonably large and of opposite sign as compared with the SQM results. As the latter force fields consistently reproduce the normal frequencies of all the molecules treated here and show an essential agreement with the experimental values for the smaller molecules, the in-plane force field of Cossart-Magos must be qualitatively incorrect. The rather large deivation between the ab initio force field and that of ref 3 has already been pointed out by Bock et al.[17] However, their unfortunate choice of the internal coordinates leads to large coupling force constants and obscures the qualitative disagreement between the two sets, leading to their conclusion that the force field of Cossart-Magos represents a "substantial improvement" over earlier suggestions.[46] Concerning the out-of-plane force field, our results disagree with those of Fukuyama et al.[45] According to our results, the coupling between the torsion and the CH wagging is very small. If their force field is transformed to our torsional coordinate, which was shown long ago to minimize coupling terms,[47] a substantial coupling is found which is doubtless an artifact of the model used. However, the difference in the force field does not lead to large differences in the normal modes, because of the large separation in the CH wagging and the torsional frequencies.

Conclusions

The results of the present study on a series of related molecules show clearly that ab initio Hartree–Fock calculations with double-ζ basis sets yield force constants which are essentially correct, showing mainly systematic errors. The latter can easily be corrected for by a simple empirical scaling. In the present case, with only six scale factors for the in-plane modes and three factors for the out-of-plane modes, a total of 115 in-plane and 41 out-of-plane frequencies are very well reproduced (standard deviation 12.3 and 6.7 cm^{-1}, respectively). We believe that the major part of the remaining deviations is due to anharmonicity and the final, scaled quantum mechanical (SQM) force fields represent the best results that can be achieved in a harmonic treatment. (Note that recent work[48] strongly suggests that even anharmonic force constants, at least the dominant terms, can be calculated with relatively high accuracy at the Hartree–Fock level. For future work, this opens the intriguing possibility of including much of the effect of anharmonicity utilizing ab initio anharmonic force constants. Indeed, calculations of this kind have already been reported for triatomic molecules.[49])

Our results allow some general conclusions concerning the transferability of force constants. From tables VIII and IX it is evident that force constants are not yet well transferable in molecules as small as the present ones, i.e., containing only four "heavy" (non-hydrogen) atoms. E.g., the force field of the vinyl fragment, present in ethylene, acrolein, and butadiene, exhibits significant differences. It seems that transferability and a related concept, the neglect of interaction between separated fragments, is justified only if the fragments are separated by at least two atoms, and possibly even more for π systems. This gives the importance of the present approach of introducing scale factors: their transferability is much better than that of the force constants themselves, as shown clearly by the fact that a few *common* scale factors could be used with success for a whole family of molecules. This result proves that the Hartree–Fock method with a limited basis set, despite its shortcomings which lead to nonnegligible systematic errors, correctly describes the differences in the force fields of similar fragments in different chemical environments.

Concerning the infrared intensities, our results show a pleasing qualitative agreement with the experimental findings; moreover, instances of "missing" infrared bands can be satisfactorily explained as having very low intensity, as in acrolein. It is clear, however, that quantitatively reliable infrared intensities require calculations of much better quality than the present ones.

The procedure and the values of scale factors estabished in this paper can be used directly to obtain good approximate force fields, normal modes, and fundamental frequencies for molecules similar to those treated here. We have already evaluated the ab initio force fields of isoprene, acetaldehyde, and hexatriene, as well as those of the cis forms of butadiene, acrolein, and glyoxal. The latter two molecules have also been dealt with by Bock et al.[17] The results, to be published separately, confirm the transferability of the scale factors.

It now seems certain that, with the help of information provided by the ab initio calculations, the force fields and normal vibrations of all reasonably simple organic molecules will be understood in the near future, after four decades of intensive experimental investigations.

Acknowledgment. This work has been supported in part by the U.S. National Science Foundation (Grant No. INT-78-19341) and the Hungarian Academy of Sciences as part of the cooperative research project of the Eötvös L. University and the University of Texas. It has also been supported in part by the Robert A. Welch Foundation.

Registry No. Glyoxal, 107-22-2; acrolein, 107-02-8; butadiene, 106-99-0; ethylene, 74-85-1; formaldehyde, 50-00-0.

---

(46) Vakhluyeva, V. I.; Sverdlov, L. M. *Izv. Vyssh. Ucheb. Zaved., Fiz.* **1968**, *11*, 146–151.

(47) Bell, R. P. *Trans. Faraday Soc.* **1945**, *41*, 293–295.

(48) Pulay, P.; Meyer, W.; Boggs, J. E. *J. Chem. Phys.* **1978**, *68*, 5077–5085.

(49) (a) Botschwina, P. *Chem. Phys.* **1979**, *40*, 33–44. (b) Botschwina, P.; Haertner, H.; Sawodny, W. *Chem. Phys. Lett.* **1980**, *74*, 156–159.