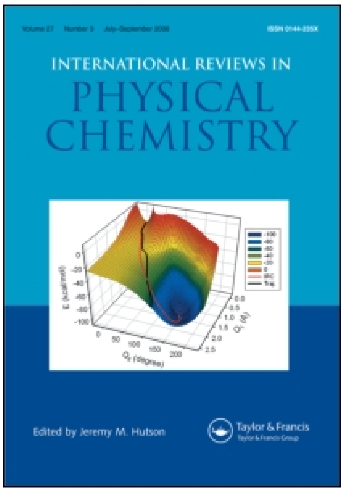

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Ab initio treatment of the Renner-Teller effect and application to various AH_2 and HAB molecules

Miljenko Perić[a]; Sigrid D. Peyerimhoff[b]; Robert J. Buenker[c]
[a] Institute of Physical Chemistry, Faculty of Science, University of Belgrade, Beograd, Yugoslavia [b] Lehrstuhl für Theoretische Chemie, Universitat Bonn, Bonnl, F.R. Germany [c] Lehrstuhl für Theoretische Chemie, Bergische Universität-Gesamthochschule Wuppertal, Wuppertal, F.R. Germany

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Ab initio treatment of the Renner–Teller effect and application to various AH_2 and HAB molecules

by MILJENKO PERIĆ
Institute of Physical Chemistry, Faculty of Science, University of Belgrade,
Studentski trg 16, POB 550, 110001 Beograd, Yugoslavia

SIGRID D. PEYERIMHOFF
Lehrstuhl für Theoretische Chemie, Universität Bonn, Wegelerstraße 12,
D-5300 Bonn1, F.R. Germany

and ROBERT J. BUENKER
Lehrstuhl für Theoretische Chemie, Bergische Universität-Gesamthochschule
Wuppertal, Gaußstraße 20, 5600 Wuppertal 1, F.R. Germany

This paper reviews *ab initio* investigations of the Renner–Teller effect in a number of triatomic molecules. The potential surfaces for nuclear motion are calculated using the MRD-CI method. The calculation of vibronic energy levels and wave functions is performed using a simple matrix method for solution of the corresponding Schrödinger equation. In this approach the potential and the kinetic energy operators are expanded in polynomial series in the bending coordinate and the hamiltonian is diagonalized in a basis consisting of products of the electronic wave functions (or their linear combinations) calculated in the Born–Oppenheimer approximation with eigenfunctions of a two-dimensional harmonic oscillator. The method allows for the treatment of large-amplitude bending vibrations and an accurate consideration of non-adiabatic effects. In the second part of this paper the effect of various approximations, as well as some interesting technical details of calculations are discussed. In the third and fourth parts of this review, a summary of results of various calculations is given. A systematic study of dihydrides of the atoms belonging to the first two rows of the Periodic Table allows the recognition of some general trends concerning the equilibrium structure and shapes of the corresponding potential surfaces. A comparison with available experimental data shows that the results of *ab initio* calculations permit a reliable representation of observed spectra. Further, the structure of yet unknown spectra can be predicted.

1. Introduction

The interpretation of an experimentally measured molecular spectrum, as well as a theoretical investigation of its structure, is necessarily based on some assumptions which allow a reduction of the complexity of the problem to a level which promises a successful interpretation. One of the corner-stones in such a theoretical analysis is the Born–Oppenheimer approximation (Born and Oppenheimer 1927). It is motivated by the experimental finding that the structure of molecular spectra can, in most cases, be interpreted in terms of a nearly complete separation of electronic and nuclear motions. A suitable mathematical formulation of this concept can be achieved by neglecting the derivatives of the electronic wave functions with respect to the nuclear coordinates, with the consequence that the molecular Schrödinger equation can be separated into its electronic and nuclear parts, coupled with each other only through a parametric dependence of the electronic wave function on the nuclear coordinates. Nonetheless, though successfully applied on a general basis, the Born–Oppenheimer approximation is known to break down in certain well specified situations.

One of the most typical and therefore important examples for the inadequacy of the separation of electronic and nuclear motion is provided by the Renner–Teller effect (Renner 1934, Herzberg and Teller 1933), predicted long before the first experimental detection of its appearance (Ramsay 1956, Dressler and Ramsay 1957, 1959). This effect is a consequence of a splitting of orbitally degenerate (at linear geometry) electronic states in the course of the bending vibrations. It is therefore characterized by a strong coupling of the electronic and bending motions and is usually accompanied by large-amplitude bending vibrations. Investigation of this phenomenon has been especially motivated by the fact that the lowest-lying electronic states of a number of triatomic molecules† are orbitally degenerate at linear geometry and that their spectra originate from transitions between the states resulting from the Renner–Teller splitting.

The original perturbative method of Renner (1934), suitable for a treatment of the weak Renner–Teller effect (in which both component electronic states have linear equilibrium geometries) has been extended and generalized by other authors (Pople and Longuet-Higgins 1958, Dixon 1965, Barrow *et al.* 1974, Jungen and Merer 1980 a, b, Köppel *et al.* 1981) who have developed more refined computation techniques, with the help of which it has become possible to achieve a very accurate fitting of experimentally measured spectra. In this review we do not intend to discuss these methods in great detail. The reader who is interested in these aspects of the general Renner–Teller problem is referred to the excellent review articles by Jungen and Merer (1964), Duxbury (1975) and Brown and Jorgensen (1983).

Until a few years ago, all applications of these approaches were based on the potential surfaces (and other relevant parameters) derived from a fitting of the available experimental data. For this reason it was not possible to make any quantitative predictions concerning the spectra prior to their actual measurement. This situation has changed in recent years with the appearance of a series of papers dealing with an *ab initio* treatment of the Renner–Teller effect. Although the accuracy of the results obtained in this manner is limited by the availability of computational time (there being no *a priori* reason to assume that there is any essential accuracy limitation in the methods themselves), we believe that these results constitute a useful contribution to the understanding of the spectra of molecules treated. In the second part of this paper a simple method for *ab initio* treatment of the Renner–Teller effect in triatomic molecules, elaborated by the present authors, is reviewed. A brief summary of the results obtained in our laboratories (Bonn, Wuppertal and Belgrade) by applying this approach is then presented in the third and fourth parts of the paper.

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† The Renner–Teller effect appears not only in triatomic, but also in all other molecules having a linear equilibrium geometry or passing through a linear conformation during their vibrations. The results of studies of the Renner–Teller effect in tetratomic molecules (Petelin and Kiselev 1972, Colin *et al.* 1979, Perić *et al.* 1961) have also been published.

2. Method for an *ab initio* treatment of the Renner–Teller effect

It is well known that the accuracy of the results obtained by means of an *ab initio* approach is dependent on the amount of computer time available. On the other hand, very useful information about a molecular system is not always characterized by a high degree of numerical accuracy, but instead carries with it an uncertainty which is confined to a reasonable, controlled range which is small enough to aid in securing a reliable identification and/or prediction of certain aspects of a given spectrum. Keeping in mind the above practical limitations of accuracy as well as the nature of the goal which should be achieved, namely to provide a basis for the reliable interpretation of the spectral data, a compromise can often be made by neglecting effects which do not play a significant role, or more precisely, which even when taken into account would not cause a significant improvement in the quality of the final results.

The electronic spectra of most triatomic molecules consist of relatively long bending progressions, and this result implies a need for considering large-amplitude vibrations of this type. Since the most prominent transitions occur almost exclusively between the lowest stretching vibration levels, these can often be treated more simply in the harmonic approximation and separated from other degrees of freedom. The coupling between the bending and the stretching vibrations can partly be taken into account in an indirect manner, e.g. using the methods proposed by Barrow *et al.* (1974) or Bunker and Landsberg (1977). Neglecting the coupling between the various vibrational degrees of freedom (or treating it indirectly as described in the above references) makes a calculation of the entire three-dimensional potential energy surface for the nuclear motion unnecessary, thereby greatly simplifying the overall computational problem; instead only three separate potential curves (for the three vibrational modes) have to be constructed, and those for stretching vibrations can be constructed from a relatively small number of points. Two rotational degrees of freedom, corresponding to the two largest moments of inertia, can also be treated separately and the third, which at linear geometry becomes the second component of the (degenerate) bending vibrations, is considered together with the bending vibration and, in the case of the Renner–Teller effect, also with the electronic motion.

An *ab initio* treatment of the Renner–Teller effect can be performed in two equivalent ways (Buenker 1978, Perić *et al.* 1983 a):

(i) (*a*) The electronic Schrödinger equation (obtained by neglecting the nuclear kinetic energy operator in the molecular hamiltonian) is solved initially for both component states using the SCF and CI method.
    (*b*) The resulting potential energy surfaces (assumed to be non-interacting) are employed for the calculation of the vibrational energy levels and wave functions.
    (*c*) The molecular hamiltonian is diagonalized in the composite basis consisting of products of the electronic and vibrational wave functions of each state (resulting from steps (*a*) and (*b*)) calculated in the Born–Oppenheimer approximation.

(ii) (*a*) The electronic Schrödinger equation is solved in the Born–Oppenheimer approximation for both electronic states as in (i).
    (*b*) The molecular hamiltonian is diagonalized in the basis formed by products of linear combinations of the electronic wave functions calculated in the Born–Oppenheimer approximation, with the eigenfunctions of a two-dimensional harmonic oscillator.

2.1. *Matrix treatment of the Renner–Teller effect*

The hamiltonian of a triatomic molecule describing the electronic motion, bending vibration and the rotations around the axis a with the smallest moment of inertia can be written in the form.

$$\begin{aligned} H &= T_{\mathrm{N}} + H_{\mathrm{e}} \\ &= -\frac{1}{2}\left[T_1(\rho)\frac{\partial^2}{\partial\rho^2} + T_2(\rho)\frac{\partial}{\partial\rho} + T_3(\rho)\frac{\partial^2}{\partial\phi^2} + T_4(\rho)\right] \\ &\quad -\frac{1}{2}\sum_i^n \nabla_i^2 - \sum_{i,a}^{n,N}\frac{Z_a}{r_{ia}} + \sum_{i<j}^{n}\frac{1}{r_{ij}} + \sum_{a<b}^{N}\frac{Z_aZ_b}{R_{ab}} \end{aligned} \tag{1}$$

where ρ represents the bending coordinate (180° − bond angle) and ϕ is the angle between the molecular plane and a space-fixed plane defining rotations around the a axis. The T_i functions, whose form depends on the choice of the moving coordinate system bound to the molecule and on the internal coordinates employed, are assumed to be dependent on ρ in order to enable a treatment of the large-amplitude bending vibrations. For the case in which the stretch–bend interaction is taken into account, these coefficients can also vary with the stretching coordinate. In the expression (1) as well as in all following formulae atomic units are used. The effect of spin–orbit coupling will be neglected entirely in this paper.

The matrix elements of the hamiltonian (1) in the basis consisting of products of the electronic wave functions[†] Ψ^α, Ψ^β and suitable rovibrational species Φ_i^α, Φ_j^β have the form

$$\begin{aligned} H^{\alpha i,\beta j} &= \langle \Psi^\alpha\ \Phi_i^\alpha | H |\ \Psi^\beta\ \Phi_j^\beta \rangle \\ &= \langle \Phi_i^\alpha | V^{\alpha\beta} | \Phi_j^\beta \rangle - \frac{1}{2}\left\langle \Phi_i^\alpha \middle| \left(T_1\frac{\partial^2}{\partial\rho^2} + T_2\frac{\partial}{\partial\rho} + T_3\frac{\partial^2}{\partial\phi^2} + T_4 \right) \middle| \Phi_j^\beta \right\rangle \delta_{\alpha\beta} \\ &\quad - \left\langle \Phi_i^\alpha \middle| {}_\rho B^{\alpha\beta}\left(T_1\frac{\partial}{\partial\rho} + \frac{1}{2}T_2 \right) + {}_\phi B^{\alpha\beta} T_3 \frac{\partial}{\partial\phi} \middle| \Phi_j^\beta \right\rangle \\ &\quad - \tfrac{1}{2}\langle \Phi_i^\alpha | ({}_\rho C^{\alpha\beta} T_1 + {}_\phi C^{\alpha\beta} T_3) | \Phi_j^\beta \rangle \end{aligned} \tag{2}$$

where

$$\left.\begin{aligned} V^{\alpha\beta} &= \langle \Psi^\alpha | H_{\mathrm{e}} | \Psi^\beta \rangle \\ {}_R B^{\alpha\beta} &= \left\langle \Psi^\alpha \middle| \frac{\partial}{\partial R} \middle| \Psi^\beta \right\rangle \\ {}_R C^{\alpha\beta} &= \left\langle \Psi^\alpha \middle| \frac{\partial^2}{\partial R^2} \middle| \Psi^\beta \right\rangle \end{aligned}\right\} \tag{3}$$

and the electronic wave functions Ψ^α, Ψ^β are assumed to be orthonormal at each nuclear geometry. Each of the V, ${}_R B$ and ${}_R C$ quantities is in principle a function of all

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[†] In general a complete set of electronic wave functions should be used, but in the present paper attention will be restricted to the use of only two of them: it is assumed that only two electronic states couple with each other. A generalization of the Renner–Teller problem to the case of several interacting electronic states has been discussed by Köppel *et al.* (*1981*).

vibrational coordinates, but in the calculations presented in this review only the ρ dependence has been given explicit consideration. In addition, the ${}_\rho B$ and ${}_\rho C$ terms are neglected entirely.

The rovibrational functions are assumed to be of the form

$$\Phi_i^\alpha(\rho, \phi) = \exp(iK\phi)\chi_i^\alpha(\rho) \tag{4}$$

where K is the total angular momentum quantum number about the a axis ($K = |l \pm \Lambda|$)†. Substituting (4) into equation (2) and integrating over the ϕ coordinate gives (after neglecting the ${}_\rho V$, ${}_\rho B$ and ${}_\rho C$ terms):

$$\begin{aligned} H^{\alpha i,\, \beta j} = {} & \left\langle \chi_i^\alpha \middle| \left[V^{\alpha\beta} - \frac{1}{2}\left(T_1 \frac{\partial^2}{\partial \rho^2} + T_2 \frac{\partial}{\partial \rho} - K^2 T_3 + T_4 \right) \right] \delta_{\alpha\beta} \middle| \chi_j^\beta \right\rangle \\ & - \langle \chi_i^\alpha | (iK\,{}_\phi B^{\alpha\beta} + \tfrac{1}{2}\,{}_\phi C^{\alpha\beta}) T_3 | \chi_j^\alpha \rangle \end{aligned} \tag{5}$$

This expression, in which ${}_\phi B^{\alpha\beta}$ and ${}_\phi C^{\alpha\beta}$ appear instead of their asymptotic values at $\rho \to 0$, represents a generalization of the relation normally used in the matrix treatment of the Renner–Teller effect (see e.g. equations (12) and (13) of Jungen and Merer 1980 a). Beginning with equation (5) two different forms of the hamiltonian matrix can be derived, depending on the choice of electronic wave functions.

(i) The real wave functions Ψ^-, Ψ^+ for both component electronic states can be used as calculated in the Born–Oppenheimer approximation. In the linear limit ($\rho \to 0$) these functions have the form $\Psi^- \sim \sin \Lambda(\theta - \phi)$ and $\Psi^+ \sim \cos \Lambda(\theta - \phi)$ (or vice versa), where θ represents the coordinate conjugate to the electronic angular momentum. Because of symmetry considerations $B^{++} = B^{--} = 0$ and $C^{+-} = C^{-+} = 0$. Furthermore, in the linear limit $B^{-+} = \Lambda = -B^{+-}$ and $C^{--} = C^{++} = -\Lambda^2$. The χ_i^α functions in (5) can be conveniently chosen as the solutions of the bending Schrödinger equation within the Born–Oppenheimer approximation

$$\chi_{il}^\alpha = \sum_v c_{iv}^\alpha R_v^l(\rho) \tag{6}$$

where

$$R_v^l(\rho) = N_v^l(\rho)(\lambda^{1/2}\rho)^l L_v^l(\lambda^{1/2}\rho) \exp(-\tfrac{1}{2}\lambda\rho^2) \tag{7}$$

represent the solutions of the radial Schrödinger equation of a two-dimensional harmonic oscillator. It has been shown (Buenker *et al.* 1981) that the value of l in

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† In all calculations presented in this paper it has been assumed that K is a good quantum number. The validity of this approximation, which considerably simplified the calculations (in this case the hamiltonian can be diagonalized in a K subspace), has been discussed recently by Carter and Handy (1984), who concluded that no significant effects are omitted if K is taken to be a good quantum number.

It has been argued (Jungen and Merer 1980 a, Carter and Handy 1984) that the vibronic levels calculated assuming K to be a good quantum number correspond to the value $J = 0$ (J being the quantum number of the total angular momentum) and that they are in this way hypothetical for $K \neq 0$. However, this problem can be considered in a slightly different way. Taking into consideration that a triatomic molecule containing at least one hydrogen atom remains nearly a symmetric top ($I_{zz} \equiv I_A \ll I_{xx} \cong I_{yy} \equiv I_B$) during its bending vibrations, its rotational hamiltonian can be approximately written in the form $H_{\text{rot}} \simeq J_z^2/2I_A + (J^2 - J_z^2)/2I_B$. The first part of this hamiltonian, having a singularity at linear geometry, is incorporated into expression (1). The second part makes a contribution to the total energy of $(J^2 - K^2)/2I_B$. This energy correction can be made after diagonalization of the hamiltonian matrix (5) or (10).

equation (7) can be chosen arbitrarily, whereby best convergence is obtained with $l < K$. If the asymptotic ($\rho \to 0$) form of the electronic wave functions is assumed, equation (7) reduces to

$$\begin{aligned} H^{\alpha i,\beta j} = & \left\langle \chi_{il}^{\alpha} \middle| V^{\alpha\beta} - \tfrac{1}{2}\left(T_1 \frac{\partial^2}{\partial \rho^2} + T_2 \frac{\partial}{\partial \rho} - l^2 T_3 + T_4 \right) \middle| \chi_{jl}^{\beta} \right\rangle \delta_{\alpha\beta}\delta_{ij} \\ & + \tfrac{1}{2}\langle \chi_{il}^{\alpha} | T_3(K^2 - l^2 + \Lambda^2) | \chi_{jl}^{\beta} \rangle \delta_{\alpha\beta} \\ & \pm iK\Lambda \langle \chi_{il}^{\alpha} | T_3 | \chi_{jl}^{\beta} \rangle (1 - \delta_{\alpha\beta}) \end{aligned} \tag{8}$$

(ii) A new electronic basis Ψ_1 Ψ_2 can be defined by a unitary transformation:

$$\left. \begin{aligned} \Psi_1 &= 2^{-1/2}(\Psi^+ + i\Psi^-) \\ \Psi_2 &= 2^{-1/2}(\Psi^+ - i\Psi^-) \end{aligned} \right\} \tag{9}$$

where Ψ^- and Ψ^+ are the exact wave functions for the lower and upper electronic state, calculated in the Born–Oppenheimer approximation. In the linear limit the functions Ψ_1 and Ψ_2 become eigenfunctions of a Π, Δ... electronic state

$$\lim_{\rho \to 0} \Psi_1 \sim \exp i\Lambda(\theta - \phi), \quad \lim_{\rho \to 0} \Psi_2 \sim \exp -i\Lambda(\theta - \phi)$$

Substituting (9) into (5) the hamiltonian matrix elements become

$$\begin{aligned} H^{\alpha i,\beta j} = & \left\langle \chi_i^{\alpha} \middle| \left\{ \tfrac{1}{2}(V^+ + V^-) - \tfrac{1}{2}\left(T_1 \frac{\partial^2}{\partial \rho^2} + T_2 \frac{\partial}{\partial \rho} - K^2 T_3 + T_4 \right) \right. \right. \\ & \left. \left. + T_3[\pm K {}_{\phi}B^{+-} - \tfrac{1}{4}({}_{\phi}C^{++} + {}_{\phi}C^{--})] \right\} \middle| \chi^{\beta} \right\rangle \delta_{\alpha\beta} \\ & + \tfrac{1}{2}\langle \chi_i^{\alpha} | [(V^+ - V^-) + \tfrac{1}{2}T_3({}_{\phi}C^{--} - {}_{\phi}C^{++})] | \chi_j^{\beta} \rangle (1 - \delta_{\alpha\beta}) \end{aligned} \tag{10}$$

The new basis does not diagonalize the electronic hamiltonian, but it does lead to the elimination of the ${}_{\phi}B$ type (non-diagonal) coupling terms. At the linear limit the matrix elements in (10) contain a diagonal term proportional to T_3 $(K \pm \Lambda)^2$ and the term $({}_{\phi}C^{--} - {}_{\phi}C^{++})$ coupling the vibronic species belonging to different electronic states vanishes.

It was shown (Perić *et al.* 1983 a, that the choice of basis (i) or (ii) has no significant effect on the results of the calculations, as long as the dimension of the basis is moderately large compared to the number of energy levels of interest. As expected, in the variant (i) the basis with $l \geqslant K$ is not quite satisfactory because the lowest K levels need a good admixture of the $R_v^{K-\Lambda}$ function (proportional to $\rho^{K-\Lambda}$, see equation (7)) and this species is comparatively difficult to represent with terms containing powers of ρ not lower than K. In another paper (Buenker *et al.* 1981), it was shown that the presence of the singularity $\sim 1/\rho^2$ in the hamiltonian matrix (5) did not cause special difficulties if the $1/\rho^2$ matrix elements were constructed by the inversion of the ρ^2 matrix. However, in spite of the fact that the equivalence between both variances has been numerically checked, all concrete calculations presented in this review have been performed using approach (ii).

It is normally assumed that there should be no significance differences in the results obtained by replacing equation (5) with its approximate counterpart (8) because of the fact that the ${}_{\phi}B$ and ${}_{\phi}C$ terms are multiplied with the function T_3 tending to $1/\rho^2$ as $\rho \to 0$, so that the contribution to the matrix elements comes predominantly from the

$\rho \rightarrow 0$ limit where ${}_{\phi}B$ and ${}_{\phi}C$ become $\pm\Lambda$ and $-\Lambda^2$ respectively. However, explicit numerical calculations (Perić *et al.* 1983 a) have shown that due to the existence of non-vanishing second derivatives with respect to ρ of functions ${}_{\phi}B$ and ${}_{\phi}C$ there appear some interesting effects as, for example, mass-dependent shifting of vibronic energy levels, which limit the accuracy of the potential curves obtained in this way by fitting the experimental data. A more detailed discussion of this problem will be given in Part 4 of this paper.

2.2. *Treatment of large-amplitude bending vibrations*

An important point in the treatment of the Renner–Teller effect is the choice of the form for the nuclear kinetic energy operator. The general form of the hamiltonian describing nuclear motion developed by Wilson (Wilson and Howard 1936, Wilson *et al.* 1955) and rearranged by Watson (1968, 1970) has the form:

$$H=\frac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}(J_\alpha-P_\alpha-L_\alpha)(J_\beta-P_\beta-L_\beta)+\frac{1}{2}\sum_r P_r^2-\frac{1}{8}\sum_\mu \mu_{\alpha\alpha}+V \qquad (11).$$

where $\mu_{\alpha\beta}^{-1}$ represent the elements of a matrix which is nearly equal to the instantaneous moment of inertia matrix, J_α and J_β are the components of the rovibronic angular momentum operator along the molecule-fixed axes, P_α and P_β are the components of the vibrational and L_α and L_β of the electronic angular momentum; P_r are the momenta conjugate with the normal coordinates and V is the potential for nuclear motion. According to the method of Wilson and Watson, $\mu_{\alpha\beta}$ and V are expanded about their values at equilibrium in a Taylor series in normal coordinates. The zero-order hamiltonian is obtained by neglecting P_α, L_α and all but the leading terms in the expressions for $\mu_{\alpha\beta}$ and V. The corresponding Schrödinger equation is then separated into an equation describing the rotational motion and $3N-6$ mutually independent harmonic oscillator equations whose eigenvalues and eigenfunctions are well known. If the higher terms in the hamiltonian are taken into account, the interaction between the vibrational and rotational motion (Coriolis interaction) and also between various vibrational modes cannot be removed and consequently it is not possible to reduce the problem in $3N-6$ dimension in this manner. This eventually then requires first a knowledge of the potential surface in $3N-6$ dimensions, i.e. the electronic Schrödinger equation would have to be solved for a great number of different nuclear arrangements. Secondly, a solution of a nuclear equation in $3N-3$ dimensions would be needed; in the case when the variational method is used that would mean that it would be necessary to solve a secular equation of dimension $\sim m^{3N-3}$, with m representing the number of basis functions for one degree of freedom. Moreover, the transformation of the potential (normally calculated as a function of some internal coordinates) into a polynomial series in normal coordinates is complicated by the fact that the transformation from internal to nuclear coordinates is nonlinear.

This general approach is especially impractical in the case when a vibrational mode (ρ) is characterized with large amplitudes, causing a slow convergence of such a Taylor series. In such situations it is much more convenient to use the approach developed primarily by Bunker and co-workers (Hougen *et al.* 1970, Bunker and Stone 1972, Bunker and Landsberg 1977, Bunker 1975). According to this method the coefficients $\mu_{\alpha\beta}$ and the potential V are expanded into Taylor series in $3N-7$ 'infinitesimal' coordinates Q_r, with ρ-dependent coefficients:

$$\left.\begin{aligned}\mu_{\alpha\beta}&=\mu_{\alpha\beta}^{\mathrm{ref}}-\sum_{\gamma,\delta,r}\mu_{\alpha\gamma}^{\mathrm{ref}}\,a_r^{\gamma\delta}\,\mu_{\delta\beta}^{\mathrm{ref}}\,Q_r+\cdots\\ V&=V_0(\rho)+\sum_r\Phi_rQ_r+\frac{1}{2}\sum_r\lambda_rQ_r^2+\frac{1}{6}\sum_{r,s,t}\Phi_{rst}Q_rQ_sQ_t+\cdots\end{aligned}\right\}\tag{12}$$

The zeroth-order hamiltonian is obtained by neglecting all but the leading terms, $\mu_{\alpha\beta}^{\mathrm{ref}}$ and $V_0(\rho)+\frac{1}{2}\sum_r\lambda_rQ_r^2$ in (12):

$$H=\frac{1}{2}\sum_{\alpha,\beta}\mu_{\alpha\beta}^{\mathrm{ref}}\,J_\alpha J_\beta+\tfrac{1}{2}\mu_{\rho\rho}J_\rho^2+V_0(\rho)\tag{13}$$

where $J=-i\partial/\partial\rho$ and $\mu_{\rho\rho}$ is the inverse of the 'reduced mass' for large-amplitude vibrations. The superscript 'ref' denotes the reference configuration, obtained when all the small-amplitude vibrational displacements are zero; this reference configurations is a function of ρ. In the papers cited (Hougen *et al.* 1970, Bunker and Stone 1972, Bunker and Landsberg 1977) are given explicit expressions for μ^{ref} and $\mu_{\rho\rho}$ as functions of ρ. The contribution of higher terms in small-amplitude (stretching) vibrations as well as the coupling between bending and stretching vibrations can be taken into account perturbationally.

Several forms of the kinetic-energy operator suitable for a treatment of large-amplitude bending vibrations have been published. The differences between them are consequences of slightly different ways in which the moving coordinate system is bound to the molecule. Three of them have been used in the *ab initio* calculations presented in this paper: (i) the $H^{(0)}$ and $H^{(2)}$ hamiltonians for AB_2 molecules by Barrow *et al.* (1974). These authors adjusted the general expression derived by Freed and Lombardi (1966) for the case when the molecule-fixed axes are the principal inertial axes, so that the effective hamiltonians $H^{(0)}$ and $H^{(2)}$ include large-amplitude bending vibrations and the rotations about the a-axis, and the second of them the leading part of the stretch–bend interaction as well; (ii) the rigid-bender hamiltonian derived by Hougen *et al.* (1970), using a reference configuration defined so that the coupling between bending and other vibrational modes is minimal. This form of the bending hamiltonian differs only in some higher terms from $H^{(2)}$ of Barrow *et al.* (1974); (iii) the semi-rigid-bender hamiltonian of Bunker and Landsberg (1977), which approximately includes the coupling between stretching and bending vibrations through the dependence of the bond lengths on the bending coordinate.

Since the bending vibrations and the rotations about the a-axis have to be considered simultaneously, the most suitable choice of coordinates is polar coordinates with ρ for bending and ϕ for the phase angle of the molecular plane with respect to a space-fixed plane. Because of the fact that the corresponding volume element of integration is in this case $\rho\,d\rho\,d\phi$, it was necessary to adjust the hamiltonian given in original references with the help of the transformation

$$H=S^{-1}H'S\tag{14}$$

where $S=(\rho/\sin\rho)^{1/2}$ in the case of the operator published by Barrow *et al.* (1974) and

$S=\rho^{1/2}$ in other cases (Hougen *et al.* 1972, Bunker and Landsberg 1977). After this step all such hamiltonians assume the form:

$$H=-\frac{1}{2}\left[T_1(\rho)\frac{\partial^2}{\partial\rho^2}+T_2(\rho)\frac{\partial}{\partial\rho}+T_3(\rho)\frac{\partial^2}{\partial\phi^2}+T_4(\rho)\right]+V(\rho) \tag{15}$$

with the coefficients $T_i(\rho)$ given explicitly elsewhere (Perić *et al.* 1982, 1983 a, Perić and Krmar 1982). At $\rho\rightarrow 0$ all three hamiltonians reduce to that of a two-dimensional harmonic oscillator:

$$H_0=\lim_{\rho\rightarrow 0}=-\frac{1}{2\mu}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\phi^2}\right)+\frac{1}{2}k\rho^2 \tag{16}$$

with $\mu=mMr^2/2(M+2m)$ for AB_2 and

$$\mu=\frac{m_1m_2m_3r_1^2r_2^2}{m_1m_3r_1^2+m_2m_3r_2^2+m_1m_2(r_1+r_2)^2} \tag{17}$$

for ABC molecules.

2.3. *Calculation of matrix elements*

By the calculation of the matrix elements (5) or (10) appearing in the vibronic secular equation, the potential and the kinetic energy terms are written in the form

$$V^{\pm}=\tfrac{1}{2}k\rho^2+V'^{\pm}, \quad T=T_0+T' \tag{18}$$

where k represents a suitably chosen parameter. $T_0+1/2k\rho^2\equiv H_0$ is the hamiltonian of a hypothetical two-dimensional harmonic oscillator whose eigenfunctions are used to form the basis for diagonalization of the hamiltonian; it contributes to the secular matrix via the diagonal terms $(v+1)(k/\mu)^{1/2}$. It has been shown (Perić *et al.* 1979 b) that the 'force constant' k determining the form of the basis functions can be chosen arbitrarily over a rather wide range without any significant effect on the final results. The potentials $V^{\pm}$ are represented by polynomials in ρ^{2n}, obtained by fitting the calculated electronic energies with the help of the least-squares procedure. The contribution of the part T' of the kinetic energy operator is accounted for by expanding the coefficients $T_i'=T_i-(T_0)_i$ into Maclaurin series in ρ and using the recursive formulas (Perić 1980):

$$\rho\frac{dR_v^l}{\partial\rho}=vR_v^l-(v^2-l^2)^{1/2}R_{v-2}^l-\rho^2R_v^l$$

$$\begin{aligned}\rho^2\frac{d^2R_v^l}{d\rho^2}=&\,v(v-1)R_v^l-(2v-3)[(v+l)(v-l)]^{1/2}R_{v-2}^l\\&+[(v+l)(v-l)(v+l-2)(v-l-2)]^{1/2}R_{v-4}^l\\&-(2v+1)\rho^2R_v^l+2[(v+l)(v-l)]^{1/2}\rho^2R_{v-2}^l+\rho^4R_v^l\end{aligned} \tag{19}$$

so that the calculation of the matrix elements of T' also reduces to the evaluation of the matrix elements of ρ^{2n}. The same concerns the calculation of the matrix elements corresponding to the ${}_{\phi}B$ and ${}_{\phi}C$ terms, which are expanded in ρ^{2n} series (for the case when they are not approximated by the asymptotic values).

The matrices of ρ^{2n} can be calculated in principle beginning with the ρ^2 matrix by matrix multiplication (Perić *et al.* 1979 b). However, due to the fact that the basis used is of finite size, the matrix for each higher degree of ρ calculated in this manner is less accurate, i.e. has a smaller number of exactly calculated elements. For this reason it is more convenient to calculate the higher-order matrices using the recursion formula

$$\rho^2 R_v^l = (v+1)R_v^l - \tfrac{1}{2}(v^2-l^2)^{1/2} R_{v-2}^l - \tfrac{1}{2}[(v+l+2)(v-l+2)]^{1/2} R_{v+2}^l \tag{20}$$

or, if matrix multiplication is employed, to begin with the ρ^2 matrix calculated in a large basis and to 'contract' each matrix of higher order by dropping the last row and column in which these inaccurately calculated elements appear.

The radial parts of the eigenfunctions of the two-dimensional harmonic oscillator, R_v^l with the same l are orthonormal: $\langle R_v^l | R_{v'}^l \rangle = \delta_{vv'}$. However, the radial functions with different l values are in general non-orthonogonal†. For calculation of some non-diagonal matrix elements proportional to $(T'^+_i - T'^-_i)$ in the case when the ρ-dependence of the bond lengths and consequently of the T'_i terms is different in the two electronic states, it is necessary to know the form of the overlap matrix $\langle R_v^l | R_{v'}^l \rangle$. For Π-electronic states ($\Lambda = 1$, $l = K+1$, $l' = K-1 = l-2$) (Perić *et al.* 1983 a):

$$\begin{aligned}
\langle R_v^l | R_v^{l'} \rangle &= -[(v-l')/(v+l)]^{1/2} \\
\langle R_v^l | R_v^{l'} \rangle &= \tfrac{1}{2}(l+l') \left(\frac{\frac{v'+l'}{2}!\,\frac{v-l}{2}!}{\frac{v'-l'}{2}!\,\frac{v+l}{2}!} \right)^{1/2}, \qquad \text{if } v' < v \\
\langle R_v^l | R_{v'}^{l'} \rangle &= 0, \quad \text{if } v' > v
\end{aligned} \tag{21}$$

For Δ electronic states ($\Lambda = 2$, $l = K+2$, $l' = K-2 = l-4$) (Perić *et al.* 1984 a):

$$\begin{aligned}
\langle R_v^l | R_v^{l'} \rangle &= \left(\frac{\frac{v-l'}{2}!\,\frac{v+l'}{2}!}{\frac{v+l}{2}!\,\frac{v-l}{2}!} \right)^{1/2} \\
\langle R_v^l | R_{v'}^{l'} \rangle &= \tfrac{1}{4}(l+l')[(l'+1)(v-l+2)-(l-1)(v'-l')] \\
&\quad \times \left(\frac{\frac{v'+l'}{2}!\,\frac{v-l}{2}!}{\frac{v+l}{2}!\,\frac{v'-l'}{2}!} \right)^{1/2}, \qquad \text{if } v' < v \\
\langle R_v^l | R_{v'}^{l'} \rangle &= 0, \quad \text{if } v' > v
\end{aligned} \tag{22}$$

A systematic analysis of the effect of various parameters (choice of k, number of expansion terms in V and T' series, size of the basis) on the calculated vibronic energy levels and a comparison with other methods for the treatment of the Renner–Teller effect (especially with these employing numerical solutions of the Schrödinger equation (Jungen and Merer 1980 a, Duxbury and Dixon 1981) has been reported by Perić *et al.* 1983 a. It was shown that the agreement between the results obtained with the very simple approach described above and those of the other methods is excellent. For example in NH_2 the largest discrepancies over a wide range of v_2 and K quantum

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† In spite of that, the basis in which the hamiltonian is diagonalized is orthonormal because of the presence of angular factors $\exp(il\phi)$.

numbers (vibronic energy values from 0–30 000 cm^{-1}) are only a few cm^{-1}, i.e. of the same order of magnitude as those between various numerical integration methods themselves.

Some comments concerning the use of the polynomials for the representation of the potentials should be made. The main question is, which order of a polynomial should be chosen for the fitting of calculated electronic energy values? A numerical analysis of this problem is presented by Perić *et al.* (1979 b, 1983 a). We repeat here only the conclusions. If the number of calculated points is small (say seven) and if they span a relatively wide range of the vibrational coordinate values (as is usually the case) there are two quite different possibilities, neither one of them being quite satisfactory: if the order of the polynomial is small (say second or third) the least square will be large (bad fitting); on the other hand a polynomial of fifth or sixth order would produce a very good fitting of the calculated points but could cause an unreliable interpolation in the regions between the explicitly calculated points. According to our experience an optimal method, especially for representation of complicated bending curves, consists in calculating a number of supplementary points with the help of the spline procedure (Perić *et al.* 1979 a) and only after that in fitting all the points (the number of them being generally 50–100) with polynomials of relatively high order (say 20th). These polynomials are flexible enough to ensure a very good fit (see Perić *et al.* 1983 a) and furthermore the large number of the fitted points prevents them from producing any unrealistic behaviour between points.

Finally, there are cases in which neither the polynomial representation of the potential and the kinetic energy terms, nor the use of the eigenfunctions of the two-dimensional oscillator as basis functions are convenient; sometimes it is necessary to consider the whole range of the values of the bending coordinate (0–180°). If in this case the variation of the inter-nuclear distances with a change in the bending coordinate is assumed, the potential remains finite for all values of ρ and cannot be well described with a polynomial series in ρ. In such (and other) cases one can use Fourier series for representing the various terms in the hamiltonian, and of course also for the vibrational functions themselves (Perić *et al.* 1983 c).

2.4. *Calculation of transition probabilities*

A problem which deserves special attention is the calculation of transition probabilities between vibronic levels. The probability for the transition between two states is proportional to the square for the corresponding transition moment

$$R_{e'v'e''v''} \sim \int \Psi'^{*}_{\mathrm{ev}} \mathbf{r} \Psi''_{\mathrm{ev}}\, d\tau_{\mathrm{ev}} = \int \Psi^{*}_{v'} \left(\int \Psi^{*}_{e'} \mathbf{r} \Psi_{e''}\, d\tau_{\mathrm{e}} \right) \Psi_{v''}\, d\tau_{\mathrm{v}} \equiv \int \Psi^{*}_{v'} \mathbf{R}_{e'e''} \Psi_{v''}\, d\tau_{\mathrm{v}} \quad (23)$$

where $\mathbf{R}_{e'e''}$ is the electronic transition moment if $e' \neq e''$ and the dipole moment otherwise. However, in the case of the Renner–Teller effect the vibrational levels cannot (except for $K=0$) be exactly attributed to one particular electronic state and in a rigorous treatment† the expression for the vibronic transition moment contains both the dipole and electronic transition moment.

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† However, for most vibronic levels, and precisely for all those not lying in the vicinity of the top of the barrier to linearity where there exists a strong coupling of the two electronic states, it is possible to make a correspondence to a particular potential surface to a good approximation.

Variance (i)

For the case in which the electronic parts of the basis functions are the component states calculated in the Born–Oppenheimer approximation, the total vibronic wave functions for the states n and m are given by

$$\left.\begin{aligned}\Psi_n&=\exp(iK\phi)\left(\Psi^-\sum_v c^-_{nv}R^l_v+\Psi^+\sum_v c^+_{nv}R^l_v\right)\\ \Psi_m&=\exp(iK'\phi)\left(\Psi^-\sum_{v'} c^-_{mv'}R^l_{v'}+\Psi^+\sum_{v'} c^+_{mv'}R^l_{v'}\right)\end{aligned}\right\} \tag{24}$$

where it is assumed that the same basis (i.e. the same l value) is used for calculation of both n and m rovibronic levels and the corresponding electronic wave functions Ψ^- and Ψ^+ represent the real functions tending to $\sin(\theta-\phi)$ and $\cos(\theta-\phi)$ respectively as $\rho\to 0$. The transition moment vector is given by

$$R_{nm}\sim \mathbf{I}\int\Psi^*_n X\Psi_m\,d\tau+\mathbf{J}\int\Psi^*_n Y\Psi_m\,d\tau+\mathbf{K}\int\Psi^*_n Z\Psi_m\,d\tau\equiv \mathbf{I}R^X_{nm}+\mathbf{J}R^Y_{nm}+\mathbf{K}R^Z_{nm} \tag{25}$$

In this equation X, Y and Z represent the axes of space-fixed system and **I**, **J** and **K** the corresponding unit vectors. Substituting the wave functions (24) into (25) one obtains.

$$\begin{aligned}R^X_{nm}=\int\exp i(K'-K)\,\phi\Bigg[&\sum_v\sum_{v'}c^-_{nv}c^-_{mv'}\,R^l_vR^l_{v'}\left(\int\Psi^-X\Psi^-\,d\tau_e\right)\rho\,d\rho\\ &+\sum_v\sum_{v'}c^+_{nv}c^-_{mv'}\int R^l_vR^l_{v'}\left(\int\Psi^+X\Psi^-\,d\tau_e\right)\rho\,d\rho\\ &+\sum_v\sum_{v'}c^-_{nv}c^+_{mv'}\int R^l_vR^l_{v'}\left(\int\Psi^-X\Psi^+\,d\tau_e\right)\rho\,d\rho\\ &+\sum_v\sum_{v'}c^+_{nv}c^+_{mv'}\int R^l_vR^l_{v'}\left(\int\Psi^+X\Psi^+\,d\tau_e\right)\rho\,d\rho\Bigg]d\phi\end{aligned} \tag{26}$$

and similarly for R^Y_{nm} and R^Z_{nm}. Assuming that the Z axis always coincides with the axis of the smallest moment of inertia†, $z\equiv a$ the transformation from the space-fixed axis system into the molecular frame x, y, z becomes

$$\left.\begin{aligned}X&=x\cos\phi-y\sin\phi=\tfrac{1}{2}[x\{\exp i\phi+\exp(-i\phi)\}+iy\{\exp i\phi-\exp(-i\phi)\}]\\ Y&=x\sin\phi+y\cos\phi=\tfrac{1}{2}[ix\{\exp(-i\phi)-\exp i\phi\}+y\{\exp i\phi+\exp(-i\phi)\}\\ Z&=z\end{aligned}\right\} \tag{27}$$

with ϕ being the angle between the molecular plane (yz) and the space-fixed YZ plane. It is convenient to make this transformation because the dipole moments and the electronic transition moment are calculated in the molecule-fixed frame. In C_s symmetry (ABC molecules) one of the component electronic states belongs to the A' and the other to the A'' irreducible representation. Since the x-coordinate transforms as

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† We are interested at present only in rotations about the axis corresponding to the smallest moment of inertia.

A'' and y and z as A' it follows that the non-vanishing components of the dipole and electronic transition moments are

$$\int \Psi^{\mp} y \Psi^{\mp}\, d\tau_e, \quad \int \Psi^{\mp} z \Psi^{\mp}\, d\tau_e, \quad \int \Psi^{\mp} x \Psi^{\pm}\, d\tau_e \tag{28}$$

the first and third including perpendicular ($K'-K=\pm 1$), the second one parallel ($K'=K$) transitions. In C_{2v} symmetry, one of the electronic states belongs to A_1 and the other to B_1 symmetry (for Π states) and x, y and z coordinates to B_1, A_1 and B_2 respectively. The non-vanishing electronic matrix elements are in this case

$$\begin{aligned} &\int \Psi^{\mp} y \Psi^{\mp}\, d\tau_e \quad \text{and} \\ &\int \Psi^{\mp} x \Psi^{\pm}\, d\tau_e \end{aligned} \tag{29}$$

both of them giving perpendicular transitions. Inserting (27) and (26) one obtains for $\mathbf{R}_{nm}$ an expression involving sums of matrix elements of the dipole and transition moment functions in the R_v^l basis.

Variance (ii)

For the case in which the electronic part of the basis consists of linear combinations of the electronic wave functions calculated in the Born–Oppenheimer approximation, the corresponding vibronic functions n and m are:

$$\left.\begin{aligned} \Psi_n &= 2^{-1/2}(\Psi^+ + i\Psi^-)\exp(iK\phi)\sum_v c_{nv}^{K-\Lambda} R_v^{K-\Lambda} + 2^{-1/2}(\Psi^+ - i\Psi^-) \\ &\qquad\qquad \times \exp(iK\phi)\sum_v c_{nv}^{K-\Lambda} R_v^{K+\Lambda} \\ &= 2^{-1/2}\exp(iK\phi)\left[\Psi^+\left(\sum_v c_{nv}^{K-\Lambda} R_v^{K-\Lambda} + \sum_v c_{nv}^{K+\Lambda} R_v^{K+\Lambda}\right) + i\Psi^-\right. \\ &\qquad\qquad \left.\times\left(\sum_v c_{nv}^{K-\Lambda} R_v^{K-\Lambda} - \sum_v c_{nv}^{K+\Lambda} R_v^{K+\Lambda}\right)\right] \\ \Psi_m &= 2^{-1/2}\exp(iK'\phi)\left[\Psi^+\left(\sum_{v'} c_{mv'}^{K-\Lambda} R_{v'}^{K'-\Lambda} + \sum_{v'} c_{mv'}^{K+\Lambda} R_{v'}^{K'+\Lambda}\right) + i\Psi^-\right. \\ &\qquad\qquad \left.\times\left(\sum_{v'} c_{mv'}^{K-\Lambda} R_{v'}^{K-\Lambda} - \sum_{v'} c_{mv'}^{K+\Lambda} R_{v'}^{K+\Lambda}\right)\right] \end{aligned}\right\} \tag{30}$$

Inserting these functions into equation (25) and proceeding in the same way as in the variant (i) one again obtains for the transition moment a sum of matrix elements involving both the dipole and the electronic transition moments, but now in a basis consisting of the R_v^l functions with various l values ($K\pm\Lambda$, $K'\pm\Lambda$).

For a comparison with experimental data it is desirable to know quantitatively how much a vibronic level belongs to a particular Born–Oppenheimer surface. In the variation (i) this is a trivial problem; one needs only to find the sums of squares of the coefficients c_{nv}^- or c_{nv}^+. If the linear basis is used (variation (ii)) the projection of the vibronic functions (equation 30) on a particular Born–Oppenheimer electronic state has to be made. For the percentage of appearance of the vibronic level n to the electronic state + and − one gets

$$\frac{1}{2}\left(\sum_{v} c_{nv}^{2K-\Lambda} + \sum_{w} c_{nw}^{2K+\Lambda} \pm 2\sum_{v}\sum_{w} c_{nv}^{K-\Lambda} c_{nw}^{K+\Lambda} \langle R_{v}^{K-\Lambda} | R_{w}^{K+\Lambda} \rangle\right) \tag{31}$$

where +, − signs in the last term correspond to the upper and the lower electronic state respectively.

2.5. *Calculation of the potential surfaces*

The potential surfaces for nuclear motion, representing the electronic energy calculated in the Born–Oppenheimer approximation have been obtained employing the MRD-CI method developed by Buenker and Peyerimhoff (Buenker and Peyerimhoff 1974 b, 1975, Buenker *et al.* 1978, Buenker 1980, 1982). A calculation of the electronic energy starts with the solution of the Hartree–Fock equations according to the Roothaan scheme (LCAO-MO method, Roothaan 1951, 1960, Huzinaga 1960, 1961). The SCF calculations have usually been performed for one electronic state only; this approach is motivated by the facts that the SCF calculations serve only to generate the molecular orbitals which are than employed for construction of the Slater determinants representing a basis for the CI calculations, and that the final results in most cases hardly depend on the choice of the MO basis at the CI level employed in this work. On the other hand, the use of the same MO set for both electronic states has the advantage that the calculation of the electronic transition moment between them is simpler than when a separate MO basis is employed for each electronic state, because of the non-orthogonality of the MOs obtained in the SCF calculations of different electronic states. The AO basis employed in the SCF calculations is generally of double-zeta quality with additional d- and sometimes f-functions centred on the heavy atoms and p-type bond functions.

A detailed description of the MRD-CI method is given in the above references; we present here only a brief summary. To begin with, a core of the MOs with lowest orbital energies (corresponding usually to the inner shells of the heavy atom) is designated and these orbitals are kept doubly occupied in all configurations. In addition, some of the MOs with highest orbital energies can be entirely excluded from further consideration. All other MOs are in principle allowed variable occupation. An important point in an MRD-CI calculation is the choice of the reference configurations, i.e. those configurations which appear with relatively large coefficients in the final electronic function (say $c_i^2 > 0{\cdot}005$). The choice of these quantities is based on prior knowledge of the system studied, on experience with similar species and finally on specific test calculations. Having chosen the reference configuration whose number is normally between 1 and 10 but sometimes also larger (up to 80), one generates the configuration basis by single and double excitations with respect to them. All the generated configurations are tested according to an energy-lowering criterion; those whose addition to the set of reference configurations causes a lowering in energy of the eigenvalues of the corresponding secular equation larger than a chosen threshold value T (a characteristic value for T is 10 μH) are included in the final secular equation. The number of selected configurations is usually in the order of 2000–10 000. A perturbation procedure enables an estimate of the CI energy corresponding to the value $T=0$. The effect of still higher excitations is taken into account by means of an extension of the perturbation formula (Langhoff and Davidson 1974):

$$\Delta E=\left(1-\sum_{i}^{\text{ref}}c_i^2\right)\left(E_{\text{ref}}-E_{\text{MRDCI}}\right) \tag{32}$$

The energy obtained if ΔE is added to the extrapolated MRD-CI value is referred to as the (estimated) full CI energy. All energy values presented in this paper correspond to that full CI limit. (It should also be noted that in the SCF and CI calculations the spatial and spin symmetry are used to reduce the dimensions of the secular equations to be solved.)

3. Summary of calculated results and discussion

In this section a review of the results of *ab initio* investigations of the Renner–Teller effect in triatomic molecules is presented. Calculations are primarily for dihydrides whose heavy atoms belong to one of the first two rows of the Periodic Table. The list of the molecules treated and their electronic configurations in the states exhibiting the Renner–Teller effect are given in table 1. These states represent generally the lowest electronic species of the corresponding molecule, exceptions being C_3 with a $^1\Sigma_g^+$ ground state and CH_2 and NH_2^+ with triplet states of lower energy. In table 2 are presented the calculated values for molecular constants together with some of the treatment details (AO basis, size of the CI secular equation). In figure 1 are shown the calculated potential curves for all dihydrides treated.

Before discussing the results, some comments should be made about the effect of the AO basis on the accuracy of the computations. The calculations are generally performed with bases including *d*-functions on heavier atoms and *s*- and *p*-polarization functions located in the middle of the bonds. Only in two cases (BH_2, NH_2) is the AO basis augmented with *f*-functions. A comparison of the results of the SCF and CI calculations shows that the potential barriers towards linearity and the T_e values are generally lower if calculated on the CI than on the SCF level of treatment, as a consequence of a poorer description of the higher states by the SCF method, and of the more effective description of electron correlation at linear geometry. There is a tendency for the *f*-functions to be somewhat more effective at very large angles so that the barrier to linearity is reduced by basis extension as well. However, it is improbable that further augmentation of the basis with still higher spherical harmonics would lead to a significant change in the computed results.

The disagreement between the calculated and experimentally deduced equilibrium distances is generally of the order of 0·01 Å. It should be noted that the equilibrium distances are not directly measured in experiments, and that in some cases a comparable large disagreement between the results obtained by various experimental studies exists. The agreement between the calculated and experimentally derived values for the equilibrium bond angle is in most cases better than 1°. In the theoretical studies under discussion relatively little attention has been paid to the determination of equilibrium geometries. The potential curves are generally calculated by varying the bending coordinates in intervals of 20° between 180° and 40–80°, while for the stretching curves a typical increment for the bond lengths is 0·2 Bohr radius. All the calculated equilibrium distances and angles given in table 2 correspond to minima of the potential curves and for this reason they can be somewhat different from the values derived experimentally, since the latter represent average values for the lowest vibrational states.

Table 1. Molecules and configurations of their states discussed in the present work.

Molecule	No. electrons		State	Electronic configurations
BH_2	7	$^2\Pi_u$	$^2A_1$	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)$
			$^2B_1$	$\ldots$ $(1b_1)$
AlH_2	15	$^2\Pi_u$	$^2A_1$	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(4a_1)^2(2b_2)^2(5a_1)$
SiH_2^+			$^2B_1$	$\ldots$ $(2b_1)$
CH_2	8	$^1\Delta_g$	$^1A_1$	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2$
NH_2^+			$^1B_1$	$\ldots$ $(3a_1)(1b_1)$
SiH_2	16	$^1\Delta_g$	$^1A_1$	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(4a_1)^2(2b_2)^2(5a_1)^2$
PH_2^+			$^1B_1$	$\ldots$ $(5a_1)(2b_1)$
NH_2	9	$^2\Pi_u$	$^2B_1$	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)$
			$2A_1$	$\ldots$ $(3a_1)(1b_1)^2$
PH_2	17	$^2\Pi_u$	$^2B_1$	$(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2(4a_1)^2(2b_2)^2(5a_1)^2(2b_1)$
SH_2^+			$^2A_1$	$\ldots$ $(5a_1)(2b_1)^2$
HNO^+	25	$^2\Pi$	$^2A'$	$\ldots$ $(6a')^2(1a'')^2(7a')$
			$^2A''$	$\ldots$ $(6a')^2(1a'')^2(2a'')$
HNF	17	$^2\Pi$	$^2A''$	$\ldots$ $(6a')^2(1a'')^2(7a')^2(2a'')$
			$^2A'$	$\ldots$ $(6a')^2(1a'')^2(7a')(2a'')^2$
C_3	18	$^2\Pi_u$	$^1B_1$	$(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(3b_2)^1(4a_1)^2(1b_1)^2(5a_1)^2(1a_2)$
			$^1A_1$	$\ldots$ $(4b_2)$

Table 2(*a*). Summary of theoretical and experimental data for various pairs of electronic states undergoing a Renner–Teller interaction.

Molecule	State	r(A°) theor.	r(A°) exp.	α (degree) theor.	α (degree) exp.	ω_1(cm^{-1}) theor.	ω_1(cm^{-1}) exp.	ω_2(cm^{-1}) theor.	ω_2(cm^{-1}) exp.	ω_3(cm^{-1}) theor.	ω_3(cm^{-1}) exp.	T_{00}(cm^{-1}) and $T_{v'-v''}$ theor.	T_{00}(cm^{-1}) and $T_{v'-v''}$ exp.
BH_2 $^2\Pi_u$	$X\,^2A_1$	1·183[66]	1·181[40]	129[66]	131[40]	2585[66]		1057[66] (1–0)	1030[40]	2863[66]		4145[66] (1–0)	4194† [40] (1–0)
	$^2B_1$	1·172[66]	1·17[40]	180[66]	180[40]	2671[66]		978[66] (3–1)/2	954[40]	2991[66]			
CH_2 $^1\Delta_g$	$^1A_1$	1·111[82]	1·11[37, 39]	102·9[82]	102·4[37, 39]			1520[69] (1–0)	1352·6[39]			8970[69] (2–0) 11450 (6–0)	7100–10800 [39] 10823[30] (6–0)
	$^1B_1$	1·074[82]	1·05[37, 39]	137·6[82]	140 ± 15[37, 39]			606[69] (4–2)/2 706 (8–6)/2	713[30] (8–6)/2				
NH_2^+ $^1\Delta_g$	$^1A_1$	1·036[73]		107·6[73]				1450[60] (1–0)				6300[60] (2–0)	
	$^1B_1$	1·023[73]		155·2[73]				1453[60] (1–0)					
NH_2 $^2\Pi_u$	$X\,^2B_1$	1·023[12]	1·024[37] 1·034[46]	102·9[12]	103·4[37] 102·4[46]	3307[12]	3221[52]	1540[12] (1–0)	1497[37] [46]	3627[12]	3300[78]	11150[12] (1–0)	11126[46]
	$^2A_1$	0·990[12]	1·004[37] 1·007[46]	143[12]	144[37] 144·2[46]	3467[12]	3325[26]	1178[12] (3–1)/2	1158[46]	3504[12]			

Molecule	State	r(A°)		α (degree)		ω_1(cm^{-1})		ω_2(cm^{-1})		ω_3(cm^{-1})		T_{00}(cm^{-1}) and $T_{v'-v''}$	
		theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.	exp.
AlH$_2$ $^2\Pi_u$	$X\,^2A_1$	1·61[57]	1·59[37]	118[57]	119[37]	1760[57]		750[57] (1–0)		2240[57]		9000[57] (1–0)	
	$^2B_1$	1·56[57]	1·53[37]	180[57]	180[37]	1910[57]		530[57] (3–1)/2		2250[57]			
SiH$_2^+$ $^2\Pi_u$	$X\,^2A_1$			119[8]				895[8] (1–0)				9200[8] (1–0)	
	$^2B_1$			180[3]				618[8] (3 – 1)/2					
PH$_2$ $^2\Pi_u$	$X\,^2B_1$	1·420[59]	1·428[37] 1·418[5]	91·1[59]	91·5[37] 91·7[5]	2330[59]	2270 ± 80 [93]	1110[59] (1–0)	1102[37] 1103[36]	2495[59]		18820[59]	18276·7[37] 18272[24]
	$^2A_1$	1·399[59]	1·403[37] 1·389[5]	122·1[59]	123·1[37] 123·2[5]	2430[59]		973[59] (1–0)	951·3[37] 949·12[5]	2660[59]			
SH$_2^+$ $^2\Pi_u$	$X\,^2B_1$	1·364[9]	1·358[32]	92·7[9]	92·9[32]	2710[9]	2380 ± 50 [84] 2485 ± 40 [75] 2516[22]	1240[9] (1–0)	1165[32] ~1000 [22]	2780[9]		18620[9]	18520[32]
	$^2A_1$	1·366[9]	1·369[32]	128·3[9]	127[32]	2620[9]	2040 ± 50 [84]	1020[9] (1–0)	~960[32] 940 ± 50 [84] 1088[34] 1080[28]	2580[9]			

HNO^{+} $^{2}\Pi$	$X\,^{2}A'$	1·07[10] (H–N) 1·16(N–O)		125[10]		2880‡[10]		890‡[10] 790[64] (1–0)		2180‡[10]		7350 (1–0)[64]	13890¶[38]
	$^{2}A''$											13833§ (9–0)	
HNF $^{2}\Pi$	$X\,^{2}A''$	1·03(H–N) [68] 1·39(N–F)	1·06(H–N) [92] 1·37(N–F)	101[68]	105[92]	3200[68]		1430[68] (1–0)	1432[45] 1441·1[54]	1000[68]	1000[45]	20600[68] (1–0)	20141[92]
	$^{2}A'$	1·01(H–N) [68] 1·34(N–F)	1·03(H–N) [92] 1·34(N–F)	123[68]	125[92]	3600[68]		1176[68] (1–0)	1081[45] 1074[92]	1262[68]			
	$^{1}B_{1}$							250[70] $(3-1)^{-}/2$	~210[35, 88,89]‖				
C$_3$ $^{1}\Pi_{u}$		1·317[76]	1·305[35]	180[76]	180[76, 37]	1185[76]	1125 [88, 89] 1086[37]		305 [88, 89]				
	$^{1}A_{1}$							450[70] $(3-1)^{+}/2$	~370[35, 88, 89]				

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† With the change of vibronic level numbering proposed in [66].
‡ Three-dimensional fit.
§ Most intense band.
¶ The band with this wavenumber is assumed to arise from HNO^{+} [38].
‖ Mean bending frequency appearing in Renner's pertubative formule.

Table 2 (*b*). Computational details of the various calculations.

Molecule	State	AO basis	No. of reference config.	No. of generated config.	Order of sec. equ. solved at threshold *T*
BH_2	$X\,^2A_1$	(1) 38 gaussians; $\alpha_d^B=0{\cdot}6$ pol: $\alpha_s=1{\cdot}3$, $\alpha_p=0{\cdot}5$	7	46250	
	$^2B_1$	(2) $+\alpha_f^B=1{\cdot}0$	5	32000	2200 ($T=5\,\mu$H)
CH_2	$^1A_1$	55; $\alpha_p^C=0{\cdot}034$, $\alpha_{d_1}^C=0{\cdot}60$, $\alpha_{d_2}^C=0{\cdot}06$	2	10000–	1300–
	$^1B_1$	pol: $\alpha_{s_1}=1{\cdot}5$, $\alpha_{s_2}=0{\cdot}10$ $\alpha_{p_1}=1{\cdot}2$, $\alpha_{p_2}=0{\cdot}15$	1	17000	2600
NH_2^+	$^1A_1$	52; $\alpha_{d_1}^N=1{\cdot}8846$, $\alpha_{d_2}^N=0{\cdot}5582$	8	20000	1870–3180
	$^1B_1$	pol: $\alpha_{s_1}=1{\cdot}8$, $\alpha_{s_2}=0{\cdot}14$ $\alpha_{p_1}=1{\cdot}5$, $\alpha_{p_2}=0{\cdot}18$	1 (7)	5500 (31900	1400–2200 17420–2100)
NH_2	$X\,^2B_1$	(1) 52; $\alpha_{d_1}^N=1{\cdot}8846$, $\alpha_{d_2}^N=0{\cdot}5582$ pol: $\alpha_{s_1}=1{\cdot}8$, $\alpha_{s_2}=0{\cdot}14$	1	(1)9715 (2)31711	2284–3357 3200–3800
	$^2A_1$	$\alpha_{p_1}=1{\cdot}5$, $\alpha_{p_2}=0{\cdot}18$ (2) 72; $+\alpha_{f_1}^N=2{\cdot}5$, $\alpha_{f_2}^N=1{\cdot}0$	1	(1)8925 (2)30145	2333–3230 3200 – 3800
AlH_2	$X\,^2A_1$	39; $\alpha_d^{Al}=0{\cdot}15$	1	1733	420–780
	$^2B_1$		1	1565	
SiH_2^+	$X\,^2A_1$	44: $\alpha_{d_1}^{Si}=0{\cdot}85$, $\alpha_{d_2}^{Si}=0{\cdot}30$	1	2458	700–900
	$^2B_1$	pol: $\alpha_p^H=0{\cdot}736$, $\alpha_{PR_y}^{Si}=0{\cdot}014$	1	2230	800–1000
PH_2	$X\,^2B_1$	48; $\alpha_{d_1}^P=0{\cdot}85$, $\alpha_{d_2}^P=0{\cdot}30$	1	6000	2000
	$^2A_1$	pol: $\alpha_s=0{\cdot}14$, $\alpha_p=0{\cdot}18$	1		
SH_2^+	$X\,^2B_1$	46; $\alpha_{d_1}^S=0{\cdot}54$, $\alpha_{d_2}^S=0{\cdot}06$	1	3281	1063
	$^2A_1$	pol: $\alpha_s=0{\cdot}8$	1	3069	1003 ($T=20\,\mu$H)
HNO^+	$X\,^2A'$	36; pol: $\alpha_s=1{\cdot}45$; $\alpha_p=0{\cdot}85$	1		
	$^2A''$	$\alpha_d=0{\cdot}63$ (N–O); $\alpha_s=1{\cdot}0$ (H–N)	1		($T=20\,\mu$H)
HNF	$X\,^2A''$	$\alpha_d^N=0{\cdot}95$, $\alpha_d^F=1{\cdot}62$	2	30000	3400–5400
	$^2A'$		2		($T=10\,\mu$H)
C_3	$^1B_1$	36;	8		
	$^1A_1$	pol: $\alpha_s=1{\cdot}25$, $\alpha_p=0{\cdot}7$	9		

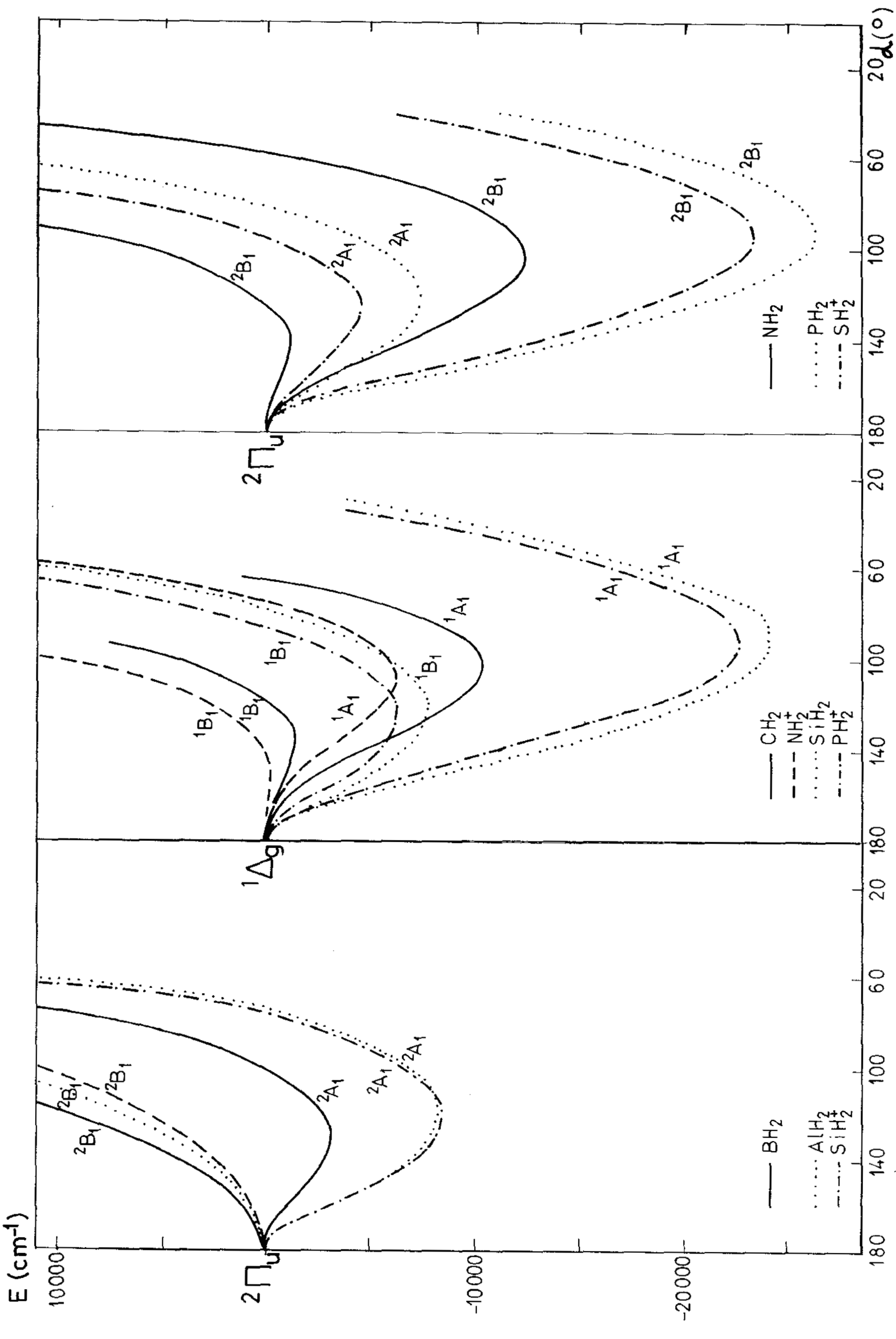

Figure 1. Bending potential for dihydrides treated in this paper calculated using *ab initio* SCF-CI methods. The SiH_2^+, SiH_2 and PH_2^+ are unpublished results by Bruna. Energy values at 180° are taken as the zero point for each pair of curves. References are: BH_2 [66], AlH_2 [57], CH_2 [82], NH_2^+ [73], NH_2 [12], PH_2 [59], SH_2^+ [9].

The calculated values for the stretching vibrational frequencies generally overestimate those derived on the basis of recorded spectra, the largest deviations being in the order of about 10%. These relatively large discrepancies are expected because the number of points determining the stretching curves is small in all cases; these curves are calculated at a particular value of the bending coordinate, in principle, that which is optimal for the equilibrium value of the stretching coordinate but not for other values, with the consequence that the resulting curves are expected to be somewhat too steep. The zeroth-order kinetic energy part of the stretching hamiltonian is used. Except for the ground state of CH_2 the agreement between calculated and experimentally obtained values for the bending frequency is considerably better; this result can be attributed to (i) a more detailed description of the bending potential curves (normally with 5–15 points), often including an optimization of the bond lengths at various values of the bending coordinate as well, and (ii) the use of kinetic energy operators suitable for a treatment of large-amplitude bending vibrations and enabling an (at least approximate) incorporation of the stretch–bend coupling. Since there is some confusion in the literature about the definition of the zero-bending frequency, we indicate in table 2 the way in which the theoretical values presented are calculated (so e.g. (3–1)/2 means the energy difference between the $v_2=3$ and $v_2=1$ levels divided by two).

Of all the quantities whose values are compared in table 2, the energy difference between the lowest-lying vibrational levels of the two electronic states (T_{00}) is the only one which can be directly measured by experiment, and the discrepancy between the experimental and theoretical results for it is most probably caused by errors in the calculations. However, in many cases the experimental value for T_{00} is not really measured but rather estimated with the help of an extrapolation procedure (see §4, BH_2); in such cases it is also possible that the determination of T_{00} is connected with an incorrect assignment of vibrational numbers in an observed progression. The agreement between theoretical and experimental results for T_{00} given in table 2 is in all cases better than 0·05 eV and still better in the case of the very extensive calculation for NH_2 (with a large basis including also *f*-functions on the N atom). All theoretical results presented in table 2 correspond to transitions to the lowest Σ ($K'=0$) vibronic level of the upper electronic state from the lowest vibronic level of the lower state from which the transitions to the Σ levels are allowed ($v_2''=0$, $K''=1$).

A rather systematic set of calculations for dihydrides AH_2 with the central atom A belonging to the first and second rows of the Periodic Table allows some general trends to be discovered concerning the equilibrium geometry and form of the potential surfaces of these species. In figure 2 are presented the heights of the barriers to linearity and the equilibrium angles for the states correlating at linear geometry with orbitally degenerage Π and Δ states of the dihydrides considered. The data for molecules whose central atoms belong to the same row are connected with lines. Isovalent species are presented along vertical directions. It is obvious that the bond angle is smaller (the molecule is more bent) and the barrier towards linearity larger if the central atom belongs to the second row. Neutral species have larger barriers and smaller bond angles than the corresponding isovalent ions. Comparing the results for a particular row one finds that the bond angle has the largest value if the central atom A lies in the third group of the Periodic Table, with similar values for the fourth and the fifth groups. The height of the potential barrier for the lower curve becomes larger in going from the third to the fifth group with the increase being much more pronounced between the third and the fourth than between the fourth and the fifth groups. In the upper state the barrier towards linearity is considerably higher for those species whose central atom belongs to

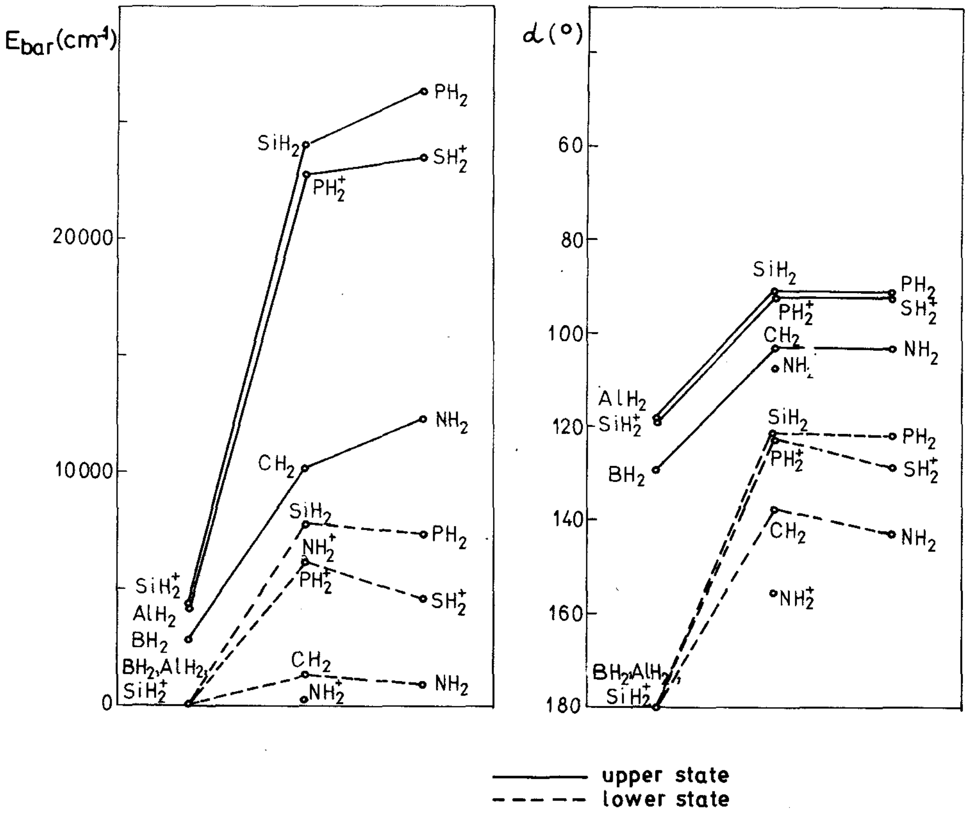

Figure 2. Calculated heights of the barrier towards linearity (left) and equilibrium bond angles (right) for dihydrides treated in the present study. Isovalent species are presented along vertical directions. Species whose central atoms succeed one another (lie in the same row) in the Periodic Table are connected with full (upper states) and dashed (lower states) lines.

the fourth group than when A is in the third group; on the other hand, the barrier height decreases somewhat in going from the fourth to the fifth group.

The relative ordering of the component states by bent geometries for a group of isovalent species is consistent with Walsh's rules (Walsh 1953, Buenker and Peyerimhoff 1974 a), e.g. the $^2A_1$ state of BH_2 is expected to have a bent geometry because it has an electron in the $3a_1$ orbital, strongly stabilized upon bending, and the $^2B_1$ state, arising from an excitation to the $1b_1$ orbital, whose energy remains practically unchanged by bending, should have a large bond angle and is actually linear. For the same reasons it is expected that the lower component of the $^1\Delta_g$ state of CH_2 should be $^1A_1$, because the corresponding electronic configuration has two electrons in the $3a_1$ orbital, while in the other state ($^1B_1$) there is only one such electron.

The accuracy of the calculated data collected in table 2 can be tested more or less directly by comparing with experiment. The situation concerning the form of the entire potential curves is different, however. The potential curves derived by fitting procedures based on known experimental data are published in some instances, but a disagreement between these results and the potential curves calculated by means of an *ab initio* technique does not necessarily mean that the latter are in error. The reason for this is that in the determination of the potential curves from experimentally measured band positions different assumptions (and approximations) can usually be made, with the result that several distinct potential curves can be derived on the basis of the same set of experimental data (see discussion in § 4). Nevertheless, generally good agreement between 'experimental' and theoretical potential curves is noted (figures 7 and 11). However, there seem to be systematic distinctions for highly bent arrangements: *ab initio* curves increase in this region more rapidly. There are several reasons that might be responsible for this effect. As already stated, this result could (but not very probably) be a consequence of the shortcomings of the AO basis employed in the calculations. A much more plausible explanation is that the form of the hamiltonian employed in the fitting of experimental data is too approximate for this geometrical region. It is clear that the interaction between bending and stretching modes must play a very important role, for example, if a molecule undergoes large-amplitude bending vibrations. Effective bending hamiltonians have been derived and employed involving (indirectly) the coupling between stretching and bending vibrations, but the question remains if any single one-dimensional hamiltonian is capable of accurately including the coupling between different degrees of freedom. Another fact hampering the construction of adequate Born–Oppenheimer potential surfaces in systems such as NH_2, PH_2, SH_2^+ etc. is the presence of a third electronic state ($^2B_2$) undergoing an avoided crossing (conical intersection) with the $^2A_1$ surface at smaller bond angles. Because of the fact that in C_s symmetry (i.e. after asymmetric stretching distortion) both these states belong to the same (A') irreducible representation and consequently the corresponding potential curves no longer cross, the shape of both must be strongly perturbed.

The above points are illustrated in figure 3 in which the calculated term values for the $^2\Pi_u$ state of NH_2 (Perić *et al.* 1983 a) are compared with those derived on the basis of experimentally obtained spectra (Jungen *et al.* 1980 a). A gradual change of the rotational K-type structure (below the barrier at 180°) into that characteristic of a two-dimensional oscillator (above the barrier), accompanied with the appearance of a minimum in the difference between successive term values for a particular K-value, can be noted. Since the calculation errors for the vibrational levels is generally of the order of 100 wave numbers (and at high v_2'' values still larger), it is clear that the *ab initio* calculations do not allow for a satisfactory description of local perturbations between neighbouring levels of the lower and upper potential surface. This is clearly seen in the energy range in the vicinity of the barrier where some irregularities in the observed spectrum are apparent which are caused by splitting of levels which would lie close to each other in the absence of the perturbation; such details are not reproduced properly in *ab initio* calculations because of the shifting of energy levels corresponding to the lower curve towards higher energies (see also figure 10).

4. Individual molecules

BH_2

Since the BH_2 radical, having only seven electrons, represents the smallest polyatomic molecule for which the Renner–Teller effect has yet been observed, *ab initio* results should be most reliable for this species and hence very good agreement between measured and calculated data could be expected. The value of T_{00} for transition between the two lowest-lying electronic states of BH_2 (correlating with a $^2\Pi_u$ state at linear geometry) reported by Herzberg and Johns (1967) as 4194 cm^{-1}, appeared, however, to contradict the results of early *ab initio* studies (Bender and Schaefer 1971, 2260 cm^{-1}, Staemmler and Jungen 1972, 3053 cm^{-1}).

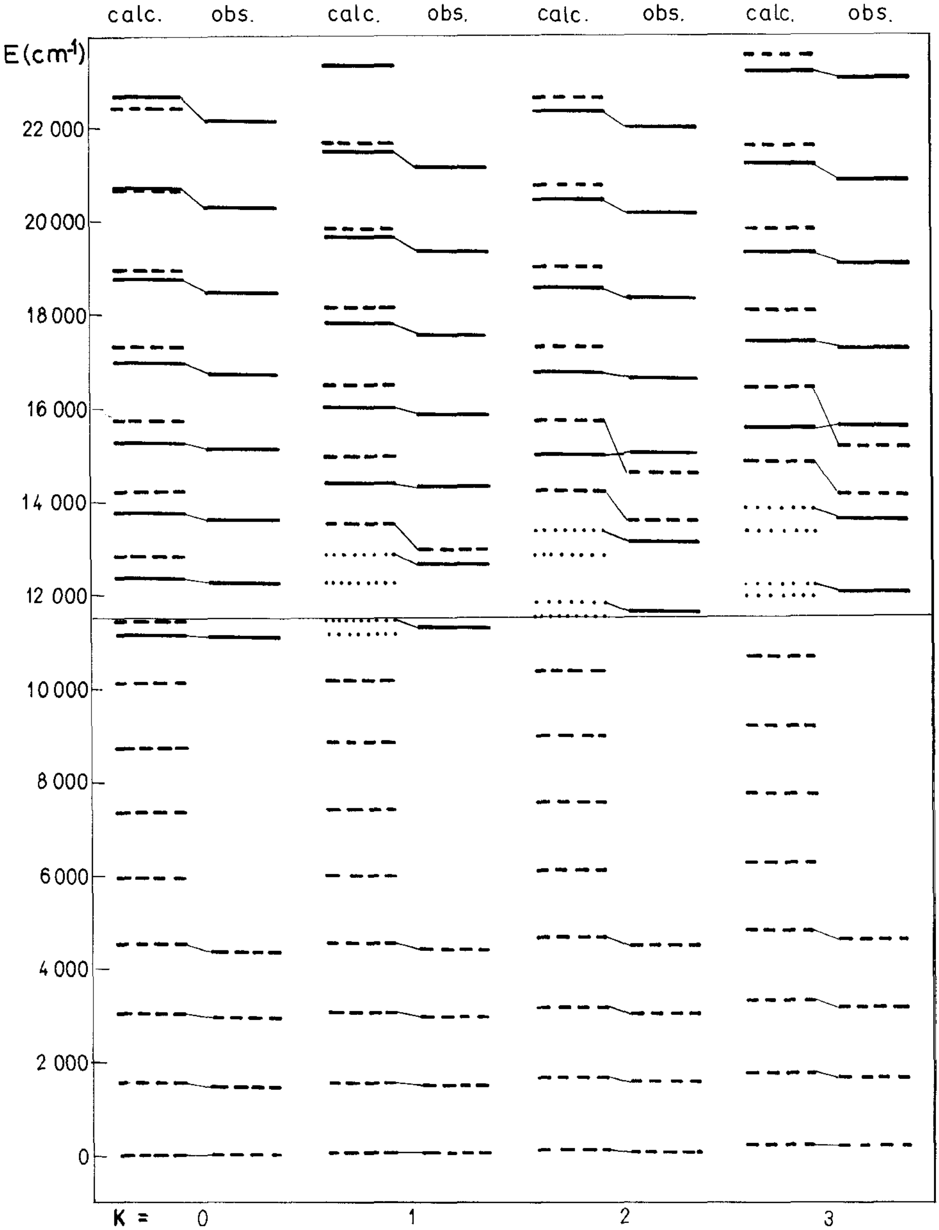

Figure 3. Comparison of calculated and observed vibronic levels in NH_2. Full lines: levels belonging to the upper potential surface ($^2A_1$); dashed lines: levels of the lower surface ($^2B_1$); dotted lines: levels which are considerably shared between both surfaces.

In order to clarify this situation extensive *ab initio* study of the $X\ ^2A_1$ and $^2B_1$ electronic states of BH_2 has been performed by Perić *et al.* (1981). The potential curves for all three vibrational degrees of freedom have been calculated by the MRD-CI method, employing an AO basis also containing an *f*-function on the B atom. The resulting potential surfaces were then used for a treatment of the Renner–Teller effect in the $^2\Pi_u$ state of BH_2, including considerations of the large-amplitude bending motion.

The calculated structural data agree to within 0·002 Å and 2° with experimentally determined bond distances and angles and the discrepancies between the computed and experimentally obtained bending frequencies are smaller than 30 cm^{-1}. For the energy difference between the minima of the both potential surfaces (T_e), a value of 3024 cm^{-1} has been obtained in the calculations with the AO basis without the *f*-functions; the presence of the latter has as a consequence of lowering the T_e value by roughly 350 cm^{-1} ($T_e = 2675$ cm^{-1}). Both results are in good agreement with those reported in earlier *ab initio* studies. Therefore, in seeking the cause of the apparent discrepancy between theoretical and experimental results, critical analysis of the interpretation of the experimental data seemed to be in order.

Herzberg and Johns (1967) observed three pairs of bands which were attributed to the bending progressions in $^{11}BH_2$ (11767·3 (Σ); 12690·3 (Π); 13640·6 (Σ) cm^{-1}) and $^{10}BH_2$ (11829 (Σ), 12760 (Π); 13717 (Σ) cm^{-1}). The authors plotted the isotope shifts between the corresponding bands against the wave number of the $^{11}BH_2$ species. Since these three points did not lie on a straight line, the slope was not determined but calculated using the ratio of the reduced masses for the bending vibrations in $^{11}BH_2$ and $^{10}BH_2$, assuming linear molecular geometry and neglecting the effect on anharmonicity on the values of the reduced masses. It was found that the slope should be 0·0077. A line of this slope which best fitted the observed points indicated that the origin of the band system should be about 4500 cm^{-1}. Taking this value into account, Herzberg and Johns fitted the observed bands in $^{11}BH_2$ (11767·3; 13640·6; 15505·9 cm^{-1}) with the formula

$$G(v_2) = \omega_2(v_2+1) + x_{22}(v_2+1)^2 + T_{00} \tag{33}$$

and found the values: $\omega_2 = 954{\cdot}65$ cm^{-1}, $x_{22} = -1{\cdot}0$ cm^{-1} and $T_{00} = 4194{\cdot}1$ cm^{-1}, corresponding to the numbering of the observed bands $v_2 = 7, 9, 11$. It should be noted that the value T_{00} corresponds to $G(v_2' = -1)$, i.e. T_{00} represents the difference between the zeroth vibrational level of the lower electronic state and the minimum of the upper potential surface (assuming it to be harmonic in the vicinity of the equilibrium geometry)†.

The lowest measured $^2\Sigma$ vibronic level in the upper state, corresponding to $v_2' = 1$, should, according to formula (33) lie at 6099·4 cm^{-1}. Herzberg and Johns found on the basis of the observed deuterium isotope shifts that such a numbering of the bands necessarily implies substantially larger frequencies for the stretching vibrations in the upper than in the lower electronic state.

Both the above conclusions, (i) $E_{v_2''=0\to v_2'=1} = 6099{\cdot}4$ cm^{-1} and (ii), an unusually large increase of the stretching frequencies in the upper state, are in clear disagreement with the results of the *ab initio* study (Perić *et al.* 1981). The best result for $E_{v_2''=0\to v_2'=1}$, obtained by employing the potential surfaces calculated with the AO basis including *f*-functions (Perić and Krmar 1982) is 4141 cm^{-1}; very similar values for the stretching frequencies of both electronic states have been found. Since it is very unlikely that the calculation error for such a small molecule could be so large (~0·3 eV in electronic energy) the interpretation of the experimental results must be questioned. The key point in this analysis is the determination of the T_{00} value. Herzberg and Johns performed the extrapolation to T_{00} using a line with a slope determined by the ratio of

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† In Herzberg's monograph (1966) a value is given for $T_0 \sim 5150$ ($\sim 4194 + 955$) cm^{-1}, representing the energy difference between the zeroth vibrational level of the lower electronic state and the hypothetical $v_2' = 0$ level of the upper state; see figure 4.

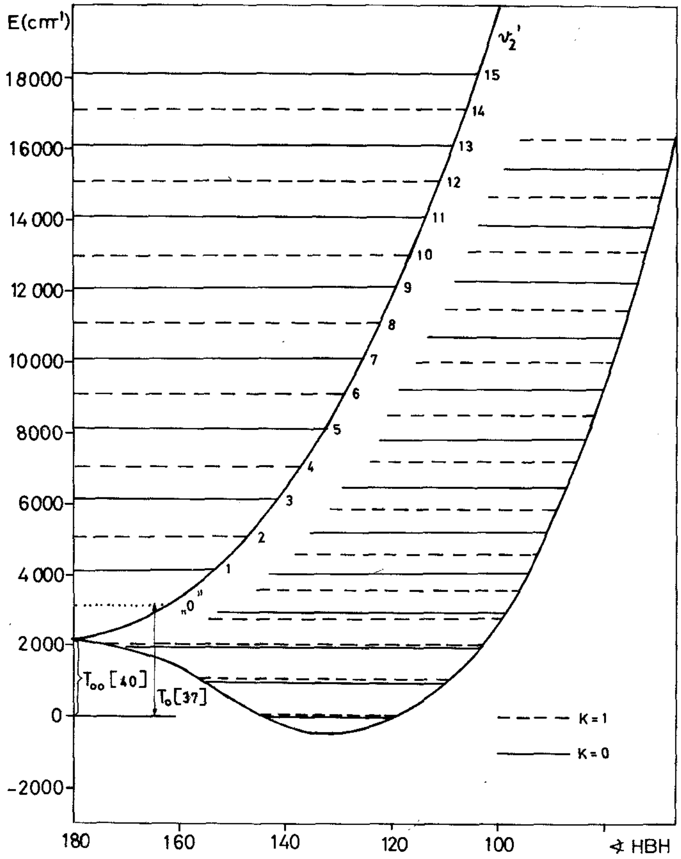

Figure 4. *Ab initio* potential surfaces for the bending vibrations in BH_2 (Perić *et al.* 1981). Calculated $K=0$ and $K=1$ vibronic levels are shown. The energy differences corresponding to the T_{00} value as defined by Herzberg and Johns (1967) and to T_0 used by Herzberg (1966) are indicated.

the reduced masses for linear geometry, assuming implicitly in this way that the vibrations also remain harmonic in highly excited bending states. However, it has been shown (Perić *et al.* 1981) that this assumption is not realistic, and that an appreciably lower value for T_{00} (2280·8 cm^{-1}) is obtained if the large-amplitude bending vibrations are taken into account. This circumstance would lead to a renumbering of the observed bands ($v_2=9$, 11, 13 instead of 7, 9, 11)†, according to which all apparent discrepancies between the experimental results and the *ab initio* calculations disappear: the first Σ level in the upper electronic state according to the formula (33) with the new numbering should lie at 4194 cm^{-1} (*ab initio* 4141 cm^{-1}, see figure 5) and the stretching frequencies in both electronic states should have similar values in accordance with theoretical predictions.

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† It should be noted that Staemmler and Jungen (1972) also questioned the numbering of observed bands proposed by Herzberg and Johns, but they did not offer a detailed explanation of the matter.

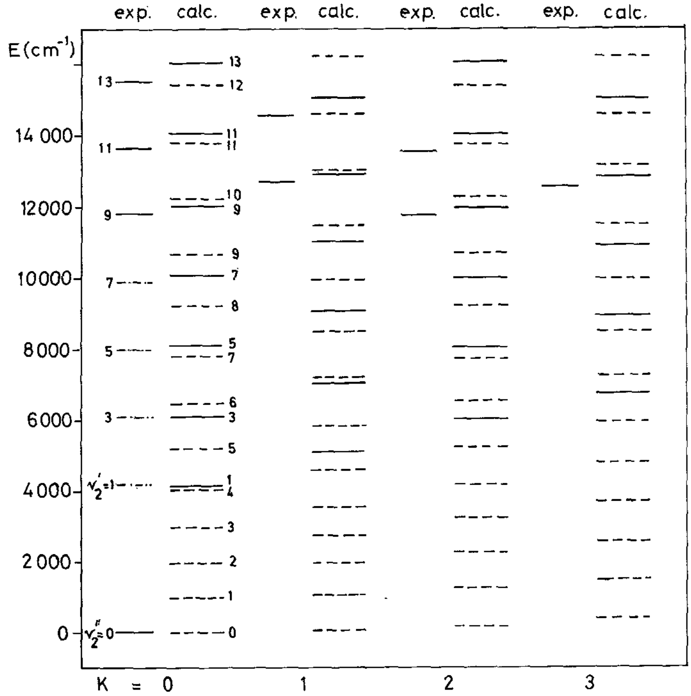

Figure 5. Calculated and experimentally derived vibronic structre of the $^2\Pi_u$ electronic state of BH_2. Calculations are performed employing an AO basis with *f*-functions. Dashed lines correspond to the levels belonging predominantly to the lower electronic state ($X\,^2A_1$), solid lines to those of the upper state ($^2B_1$), dash-dot lines denote the positions of the bands not directly observed but calculated from equation (33). Observed bands are renumbered as proposed by Perić *et al.* (1981).

AlH_2

The only experimental information concerning the spectrum of AlH_2 are those given by Herzberg (1966). The results of *ab initio* calculations performed with a rather small AO basis (without *f*- and other polarization functions) (Nestmann and Perić 1984) agree well with these data. Further, other molecular constants, not available experimentally, as well as the positions of vibration-rotational levels and the intensity distributions in band progressions have been calculated.

CH_2

To our knowledge the first *ab initio* treatment of the Renner–Teller effect in a Δ electronic state has been performed for the CH_2 molecule (Perić *et al.* 1984 a). The results (figure 6) are in reasonably good agreement with the corresponding experimentally obtained data (Duxbury 1982, Ashfold *et al.* 1982).

NH_2^+

NH_2^+ represents one of the free radicals which is interesting from an astrophysical point of view. *Ab initio* calculations are in this case especially desirable because of the absence of any experimental information concerning its spectrum. It has been found (Peyerimhoff and Buenker 1979 a) that the spectrum of NH_2^+ should be very complicated because of the existence of a number of electronic states in a relatively

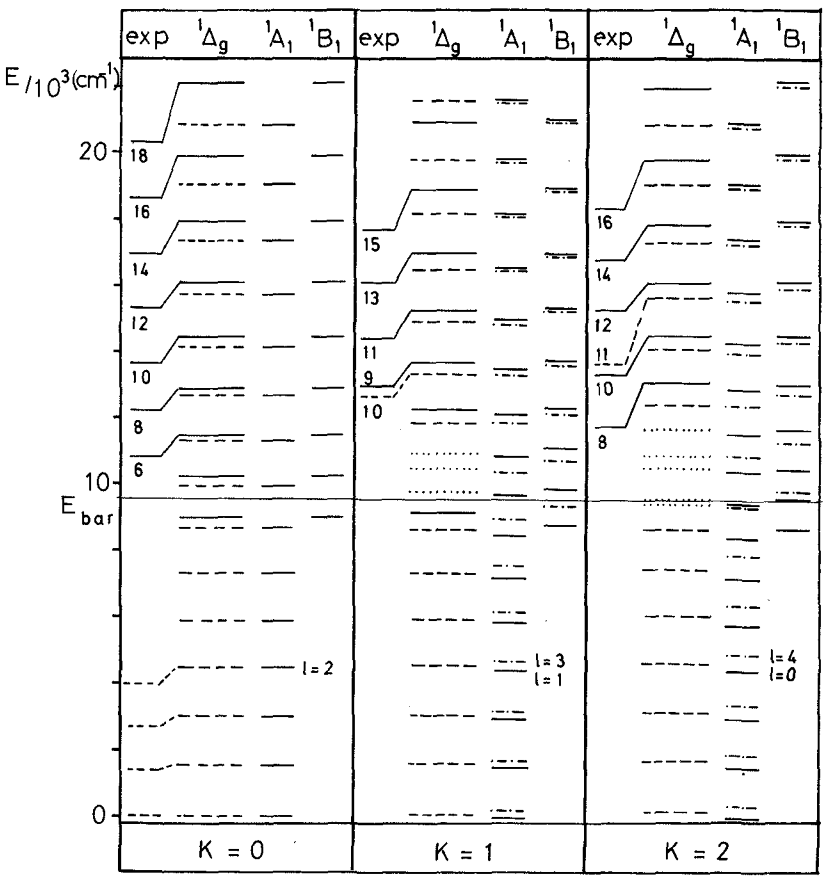

Figure 6. Comparison of the calculated vibronic energy schema in the $^1\Delta_g$ state of CH_2 (Perić *et al.* 1984 a) with those obtained on the basis of experimental results (Duxbury 1982). Dashed lines indicate the levels belonging predominantly to the lower Born–Oppenheimer electronic state, solid lines the levels corresponding to the upper state. The levels appreciably shared by both electronic states are denoted with dotted lines. Right: vibrational levels of the component electronic states obtained by neglecting the Renner–Teller coupling.

narrow energy region, including various interactions between these states (avoided crossings, Renner–Teller effect etc.). The Renner–Teller effect in the lowest singlet state $^1\Delta_g$ has been studied by Perić *et al.* (1984 b). It was found that in the $^1B_1$ upper state the barrier toward linearity was only 220 cm^{-1}, so that in the upper state all vibrational levels lie above the barrier.

NH_2

NH_2 is probably the most frequently studied molecule exhibiting the Renner–Teller effect (e.g. Ramsay 1956, Dressler and Ramsay 1957, 1959, Pople and Longuet-Higgins 1958, Dixon 1965). Extensive *ab initio* calculations with an AO basis including *f*-functions located at the N atom, as well as the *s*- and *p*-type bond functions, have been published by Buenker *et al.* (1981). In order to get a basis for a more refined treatment of the large-amplitude bending vibrations, the bending curves for the $\tilde{X}\,^2B_1$ and $\tilde{A}\,^2A_1$

states have been calculated by optimizing the N–H distances at a number of values of bond angle. The dependence of the bond distances (figure 7) as well as the ${}_{\phi}B$ and ${}_{\phi}C$ terms (figure 8) on the bending coordinate have been computed.

The overall agreement between the theoretical predictions and the data obtained experimentally is very good. Calculated equilibrium bond lengths and angles agree within 0·01 Å and 1° of their observed values and computed vibrational frequencies agree to within 3% of their available measured counterparts. The calculated T_e value for the $\tilde{A}\,{}^2A_1$–$\tilde{X}\,{}^2B_1$ transition of 11350 cm^{-1} is in excellent agreement with the value based on an empirical fitting procedure (Jungen *et al.* 1980 a) of 11294 cm^{-1}. The theoretically predicted vibronic structure of the electronic transition agrees very well with the observed spectrum (figure 3) and the intensity distributions in the band progressions are in almost quantitative agreement with the experimental findings

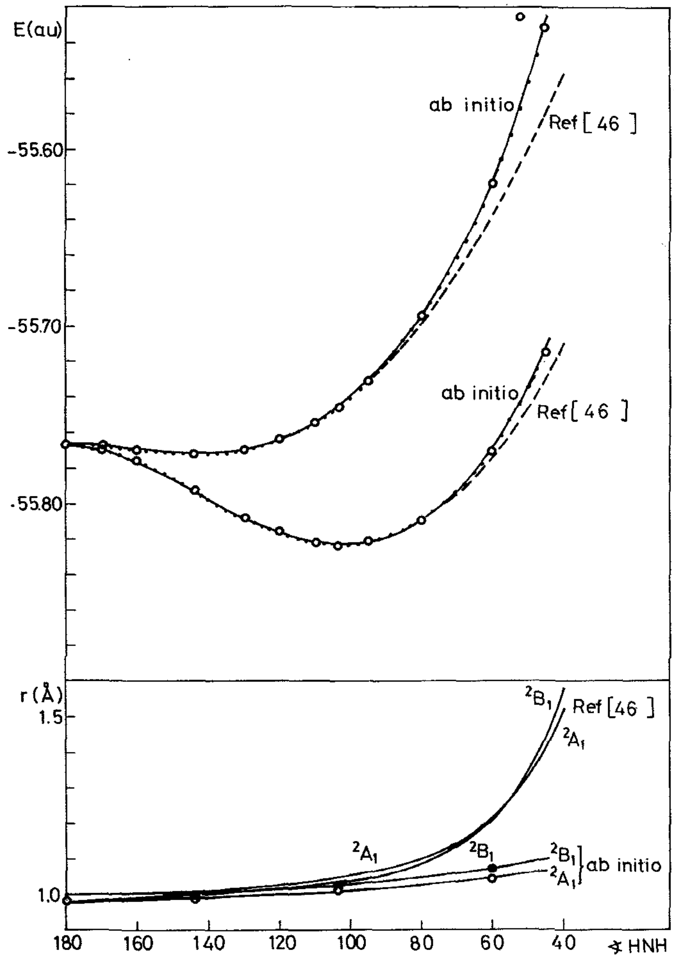

Figure 7. Top: *ab initio* potential surfaces for bending vibrations in the ${}^2\Pi_u$ state of NH_2 (solid lines) (Buenker *et al.* 1981). ○, actually calculated points corresponding to the optimized N–H distances for each angle;…, points generated employing the spline procedure. Dashed lines denote the potential curves deduced by Jungen *et al.* (1980 a) on the basis of experimental findings. Bottom: calculated and experimentally deduced dependence of the N–H distances in NH_2 on the bending coordinate.

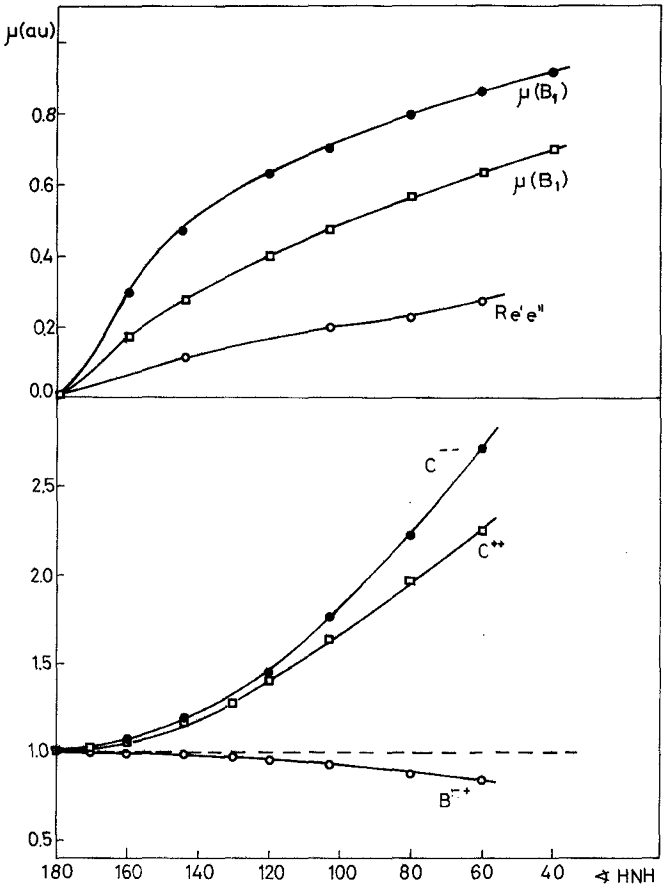

Figure 8. Variation of dipole moments, electronic transition moment (top) and non-adiabatic matrix elements

$$_\phi B^{+-} = \left\langle \Psi^- \middle| \frac{\partial}{\partial\phi} \middle| \Psi^+ \right\rangle \quad \text{and} \quad _\phi C^{\mp\mp} = \left\langle \Psi^\mp \middle| \frac{\partial^2}{\partial\phi^2} \middle| \Psi^\mp \right\rangle$$

(bottom) for the two lowest electronic states of NH_2 ($X\,^2B_1$ and $A\,^2A_1$) with change in the bending coordinate.

(figure 9). However, in spite of this general agreement, there exist some discrepancies between the theoretical results and those obtained directly in experiments and/or derived on the basis of experimental findings. Since these discrepancies concern not only the NH_2 radical but are systematic in nature, they merit a brief discussion.

As already mentioned in § 3 of this paper, the poorest agreement between the *ab initio* and (direct) experimental results occurs with respect to the positions of higher vibrational levels; the calculated term values are systematically higher (figure 3). This finding is a consequence of the fact that the potential curves derived on the basis of observed bands are generally flatter in the region of large values of the bending coordinate ρ (i.e. small bond angles) than those obtained in *ab initio* calculations. As already discussed in § 3, however, this situation does not necessarily imply that the *ab initio* curves are too steep. Various potential curves can be obtained on the basis of the same set of experimental observations, depending on the form of the assumed

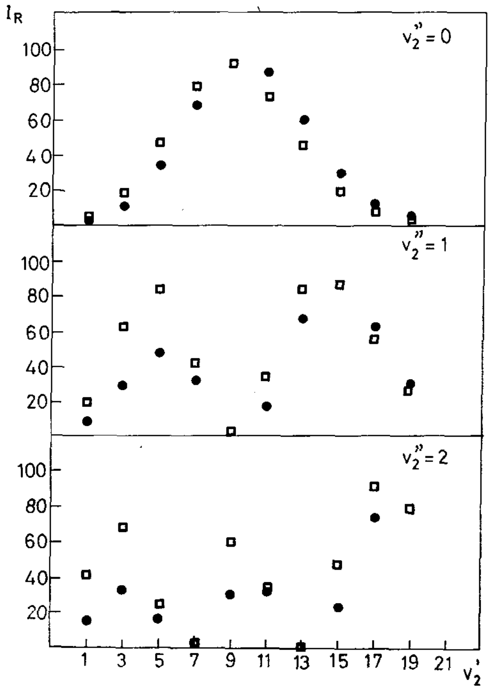

Figure 9. Comparison of *ab initio* results (□) and those derived by Jungen *et al.* (1980 a) on the basis of experimental data (●) for the intensity distribution in the bending progress of the $\tilde{A}\ ^2A_1$–$\tilde{X}\ ^2B_1$ transition in NH_2. The calculated $R_{e'v'e''v''}$ values are normalized to agree with the maximum of intensity of $v_2'' = 0$ in Jungen *et al.* (1980 a).

hamiltonian (kinetic energy), on the assumptions about the relative locations of other neighbouring electronic states, etc. This point is illustrated in figure 7, where a comparison is made between the *ab initio* potential surfaces for bending vibrations and the ρ-dependence of the bond lengths and the corresponding quantities obtained via fitting of the experimental data (Jungen *et al.* 1980 a). It can be seen that at large values of ρ the discrepancies between the two sets of results for both potential surfaces and bond lengths become rather pronounced, whereby at least the 'experimental' N–H distances cannot be realistic. In spite of this circumstance, the vibronic energy levels calculated using the 'experimental' potential curves and bond lengths (which enter into the hamiltonian through the kinetic energy operator) reproduce the observed spectrum very well. However, this is not surprising because the same assumptions are made in deriving the potential surfaces and bond lengths from available experimental data as in the calculation of the vibronic levels themselves.

A much more serious reason to question the reliability of the *ab initio* potential surfaces seems (at least at first glance) to be the discrepancy between the calculated positions of the bands and those directly observed. However, this result can also be caused by (i) inadequacy of the one-dimensional treatment of the bending vibrations, since it cannot be expected that the stretch–bend interaction is exactly treated by a one-dimensional hamiltonian, and (ii) the presence of other electronic states which can interact with the Renner–Teller components, thereby perturbing their potential surfaces (Bell and Schaefer 1971, Peyerimhoff and Buenker 1979 b). The effect of other states is included automatically in the 'experimental' potential surfaces, but is totally absent in the *ab initio* calculations under discussion.

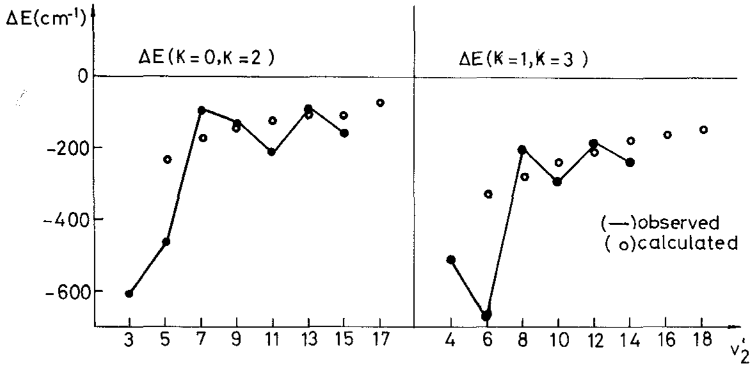

Figure 10. Comparison betweeen calculated and observed $K=0$–2 and $K=1$–3 vibronic splittings in the $A\,^2A_1$ state of NH_2 as functions of the vibrational quantum number.

The calculated energy differences between the $K=0$, $K=2$ and $K=1$, $K=3$ levels corresponding to the same vibrational quantum numbers are presented in figure 10, together with the experimental data. Since the *ab initio* calculations are not capable of getting the relative spacings of the respective unperturbed $A\,^2A_1$ and $X\,^2B_1$ vibronic levels to an accuracy of better than 100 cm^{-1}, it is not surprising that they do not allow for a satisfactorily detailed description of the strong local perturbations. However, when the local perturbations are not present there is good agreement between the experimental and theoretical results. The same conclusion applies to the intensity distributions presented in figure 9.

The effect of replacing the ${}_{\phi}B$ and ${}_{\phi}C$ terms (figure 8) by their asymptotic values $\pm\Lambda$ and $-\Lambda^2$ respectively has been analysed by Perić *et al.* 1983 a). It has usually been argued that the above approximation does not diminish the accuracy of the calculated vibronic levels because ${}_{\phi}B$ and ${}_{\phi}C$ appear in the hamiltonian matrix multiplied with the term T_3 having a singularity as $\rho\to0$, causing their contribution to be strongly weighted towards the linear geometry for which ${}_{\phi}B$ and ${}_{\phi}C$ really become $\pm\Lambda$ and $-\Lambda^2$. However, it was shown (Perić *et al.* 1983 a) that the higher terms in the series ${}_{\phi}B=f(\rho)$ cause a shifting of the positions of the vibronic levels by a magnitude of order 1·0 cm^{-1}. This correction is proportional to the K-value and has opposite sign for the two component electronic states. So it represents an effect which cannot be safely neglected when high accuracy is desired. The higher terms in the diagonal ${}_{\phi}C$ terms cause a practically parallel shift of all the vibronic levels, but its magnitude is not the same for both Born–Oppenheimer potential surfaces. In NH_2 the $X\,^2B_1$ levels show an increase of 17 cm^{-1}, for example, while all $A\,^2A_1$ counterparts are shifted by about 14 cm^{-1}. In this way the transition energies between X and A vibronic levels are decreased by roughly 3 cm^{-1} as a result of making this improvement in the theoretical treatment. The diagonal ${}_{\phi}C$ terms can be incorporated into the Born–Oppenheimer potentials but, because of the fact that they also appear multiplied with a mass-dependent factor T_3, the potentials corrected in this manner are not isotopically invariant. On the basis of this analysis it can be concluded that the replacement of ${}_{\phi}B$ and ${}_{\phi}C$ terms by their asymptotic values causes an error of the magnitude of 3–5 cm^{-1}, so that the reliability of the description of local perturbations and similar effects without knowledge of the explicit dependence of ${}_{\phi}B$ and ${}_{\phi}C$ terms on ρ can suffer from omission of such details.

PH_2, H_2S^+

The results of an *ab initio* study of the structure of two lowest-lying electronic states of the PH_2 radical, correlating with the $^2\Pi_u$ state, have been reported by Perić *et al.* (1979 a). Generally very good agreement between the theoretical and available experimental data can be noted. This conclusion is especially valid for progressions in the bending vibrations in absorption spectra, for which the observed and calculated positions of the bands as well as the appearance of the associated intensity distribution are very similar to one other. Some experimentally undetermined structural parameters (frequencies for stretching vibrations) have also been calculated. In another paper (Perić 1980) the results of an *ab initio* treatment of the Renner–Teller effect in the $^2\Pi_u$ state of PH_2 have been described.

Bruna *et al.* (1980) have also reported potential surfaces for the two components of the $^2\Pi_u$ state of H_2S^+. A comparison was made between the *ab initio* potential curves and those deduced by fitting the experimental data (Duxbury *et al.* 1972, Dixon *et al.* 1972). It was found that the agreement between the two sets of potential surfaces in the bond-angle range 180°–80° was very good. The distinctions become relatively large only at very strongly bent geometries (as in the case of NH_2). These discrepancies were explained by (*a*) the fact that the *ab initio* curves were calculated at fixed bond lengths and (*b*) that the interaction between the upper $^2A_1$ state and a third ($^2B_2$) state play a significant role at small angles (figure 11), both states assume the same (A') symmetry at the lower C_s symmetry which is reached by asymmetric distortions and therefore the corresponding potential surfaces strongly perturb each other in this region. The presence of the $^2B_2$ state was ignored in the *ab initio* calculations for the $^2A_1$ potential surface, so that relatively poor agreement between the theoretical and 'experimental'

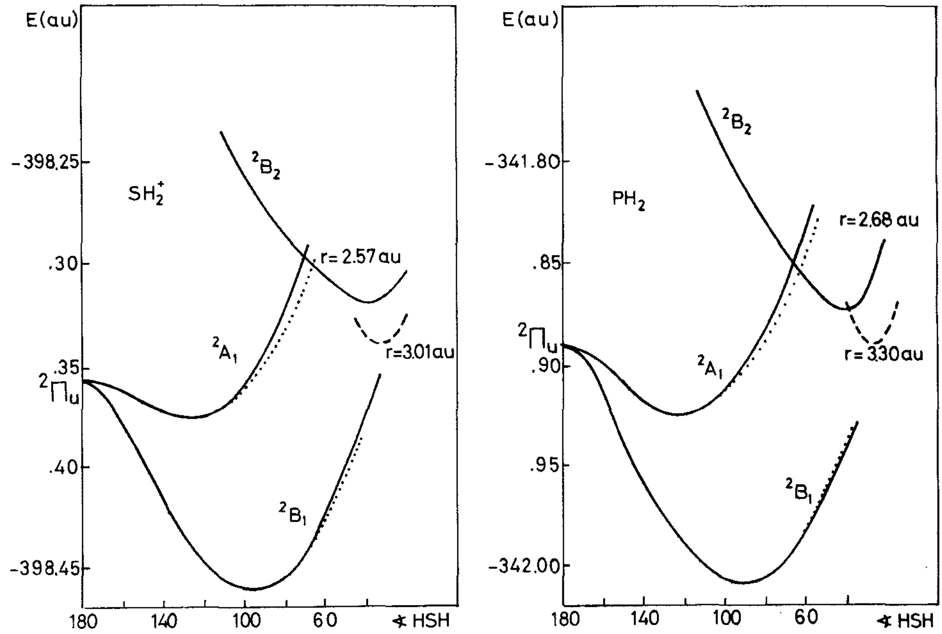

Figure 11. Calculated CI bending curves for the three lowest states in H_2S^+ (Bruna *et al.* 1980) and PH_2 (Perić *et al.* 1979 a). The dashed lines indicate the $^2B_2$ curves for the optimized SH (PH) distances. The circles are data which are obtained by using the analytic functions (Duxbury *et al.* 1972, Barrow *et al.* 1974) which give the best fit to the experimental data.

potentials is not surprising. Similar conclusions result from a comparison of the *ab initio* surfaces for PH_2 (Perić *et al.* 1979 a) and the experimentally deduced ones (Barrow *et al.* 1974). As in the case of PH_2, the positions of the observed bands and the intensity distribution in the bending progression in the absorption spectrum of H_2S^+ are reproduced quantitatively. An *ab initio* study of the Renner–Teller effect in H_2S^+ has been presented by Perić and Krmar (1980).

HNO^+

HNO^+ is another interesting free radical of interest in astrophysics because it is believed to be present in interstellar space. Herzberg (1971) indicated that the absorption spectrum observed at 7200 Å (1·73 eV) could be caused by an electronic transition in HNO^+. This assumption was supported by *ab initio* calculations (Marian *et al.* 1977, McLean *et al.* 1978, Bruna and Marian 1979), giving for the vertical transition between the ground $1^2A'$ and the lowest-lying excited state $1^2A''$ of HNO^+ the energy values of 1·78 (McLean *et al.* 1978) and 1·65 eV (Bruna and Marian 1979). In order to give a more definite answer to the question whether the observed spectrum at 7200 Å really originates from HNO^+, a study of the vibrational and rotational structure of the $1^2A''$–$1^2A'$ transition has been performed (Perić *et al.* 1982). The two electronic states in question correlate at linear molecular geometry with a $^2\Pi$ state and thus exhibit a Renner–Teller effect. The calculations of the vibronic levels have been performed employing the bending potential curves obtained with a relatively small AO basis without atom-centred *d*- and *f*-functions and calculated at constant internuclear distances (i.e. the stretch–bend interaction has been completely neglected). Nevertheless, on the basis of experience with similar systems it could be expected that the theoretical predictions should be rather reliable. The most intense Σ bands in absorption are predicted to appear at 10666 cm^{-1} ($v'_2=5$), 12556 cm^{-1} ($v'_2=7$), 13833 cm^{-1} ($v'_2=9$) and 15411 cm^{-1} ($v'_2=11$), with intensities proportional to 0·149, 0·300, 0·301 and 0·161 respectively. The strongest of these bands ($v'_2=9$) should have a wavelength of 7230 Å, in seemingly strong support of Herzberg's assumption. It should be noted, however, that such excellent agreement between the observed and calculated band positions must be assumed to be accidental; because of the shortcomings in the AO basis and the approximations made in the calculations, the calculation error is usually expected to be of the order of 0·2 eV.

HNF

An *ab initio* study of the two lowest-lying states of HNF, $X\ ^2A''$, $A\ ^2A'$ ($^2\Pi$) has also been reported by Perić *et al.* (1983 b). The main features of the observed spectrum of this system are reproduced and some unknown molecular constants calculated. The general agreement between the results of the calculations and available experimental data is satisfactory. However, some disagreement in the calculated and observed intensity distributions (Woodman 1970, Lindsay *et al.* 1979) are present. These discrepancies can hardly be explained solely in terms of errors in the calculations; at the same time, the intensity distribution found experimentally seems to be quite consistent with the equilibrium geometries also derived from experimental data.

C_3

The C_3 molecule represents a classical example of the weak Renner–Teller effect characterized by linear equilibrium geometries for both component electronic states. In this case it is impossible to reproduce even the coarse structure of the spectrum without

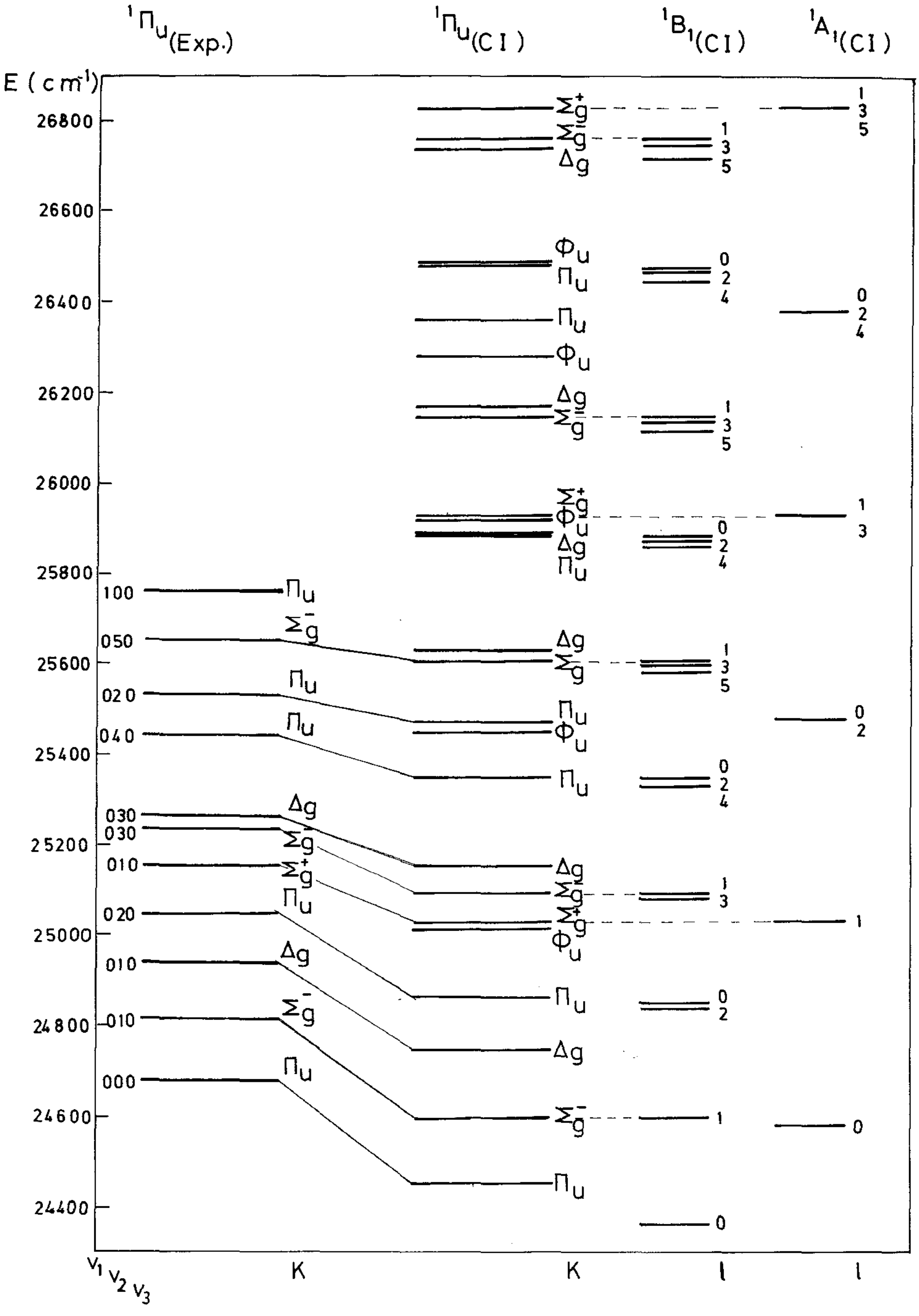

Figure 12. Comparison of the calculated vibronic term values (Perić and Radić-Perić 1979) for the $^1\Pi_u$ state of C_3 (second column) with the experimentally obtained values (Gausset *et al.* 1965). The results presented in the third and fourth columns correspond to calculations in which vibronic coupling is neglected.

considering the vibronic interaction. Although based on the potential surfaces calculated using a small AO basis (Radić-Perić *et al.* 1977), the results of an *ab initio* treatment of the Renner–Teller effect in the $^1\Pi_u$ state of C_3 (Perić and Radić-Perić 1979) are in good agreement with experimental findings (figure 12).

5. Conclusion

A summary of the usual uncertainties in the *ab initio* results presented in this review is given in table 3. The magnitude of the calculation errors are the consequence of the general philosophy (and corresponding compromises) applied: to obtain as much useful information as possible concerning molecular spectra, spending as little computer time as possible. In extreme cases only the bending potential curve is constructed (on the basis of 5–7 points calculated at fixed internuclear distances). In such cases quite close agreement between theoretically and experimentally derived structural data cannot be expected. As discussed in §§ 3 and 4 of this review enlargement of the AO basis, optimization of the internuclear distances for various bond angles, approximate consideration of the coupling between different vibrational degrees of freedom, etc. generally leads to a diminution of the computational error. On the basis of explicit consideration of the effects of various approximations, however, it can be concluded that there exist definite limits in the overall accuracy, including an explicit treatment of the coupling between various degrees of freedom as well as interactions between neighbouring electronic states, etc.

Table 3. Error estimates for calculated data in this work.

Quantity	Calculating error
Equilibrium internuclear distance	0·01 Å
Equilibrium bond angle	1–2°
Electronic transition energy	0·05 eV
Stretching vibrational frequency	100–200 cm^{-1}
Bending vibrational frequency	50 cm^{-1}
Quantum number of the most intensive band in a progression	0(±1)

In this connection the important question can be raised as to whether it is really necessary to achieve experimental accuracy in such calculations to make them useful. In our opinion, a theoretical and an experimental study of a molecular spectrum should be complementary to one another rather than competitive. It is quite difficult to calculate the position of a band with the same accuracy with which it can be measured; on the other hand, it is sometimes very difficult to make a correct assignment of the observed bands, or to derive the values of certain structural parameters when the necessary experimental information is not available in sufficient quantity (e.g. frequencies of stretching vibrations). In these cases, as well as whenever insight into the mechanism of various interactions is sought, the *ab initio* calculation can be indispensable. In summary it seems fair to say that experimental and theoretical means do not exclude one another in such investigations, but on the contrary should be employed in parallel in attempting to form an accurate picture of the molecules responsible for observed spectral phenomena.

Acknowledgments

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