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This paper reports an extension of our method, introduced several years ago, for the variational treatment of the rovibronic levels of Renner–Teller triatomic molecules. A more complete treatment now introduces the effect of electron spin. Thus new terms enter the Hamiltonian because (a) the total-angular-momentum operator $\hat{J}$ is replaced by $\hat{J} - \hat{L} - \hat{S}$ in the kinetic-energy operator, and (b) spin–orbit effects must be introduced. Here we include the latter through a semi-empirical form $A\hat{L} \cdot \hat{S}$. Expansion functions having the correct symmetry $(\Sigma_g^+, \Sigma_u^+, \Sigma_g^-, \Sigma_u^-)$, for $D_{\infty h}$ molecules are derived. Hence the present approach takes into account the full dimensionality, anharmonicity and rotation–vibration coupling, as well as the coupling of all relevant angular momenta. This is particularly important for open-shell molecules and/or for electronically degenerate states. For the $\tilde{X}\,^2\Pi_g$ electronic ground state of the CO_2^+ ion the spin–rotation and spin–orbit split Renner–Teller levels have been calculated using three-dimensional electronic potential-energy functions, for both Renner–Teller surfaces, derived from *ab initio* computation. The fundamental frequencies are in very good agreement with the available experimental data. In particular, the low antisymmetric stretch frequency and its negative anharmonicity are reproduced. Previously it had been postulated that this anharmonicity was due to a vibronic coupling between the $\tilde{X}\,^2\Pi_g$ and $\tilde{A}\,^2\Pi_u$ states; these calculations, however, show that it arises naturally from accurate representations of the adiabatic surfaces.

1. Introduction

The variational method for the determination of vibrational ($J = 0$) levels of triatomic molecules is now established. Some 15 years of intense studies have yielded the correct kinetic-energy operators for appropriate internal coordinates, using well-chosen expansion functions [1–15]. It is now recognised that highly excited vibrational levels may be determined (up to $15\,000\,\mathrm{cm}^{-1}$), and, by choosing a sufficient number of expansion functions, these eigenvalues may be determined to any accuracy. A most

important contribution of this work is that a comparison of these eigenvalues with experimental vibrational levels represents a rigorous test on the accuracy of the potential surface that is being used. Some work has also been reported on the determination of $(J = 0)$ vibrational levels of tetraatomic molecules, using the same methodology [8, 11]. Furthermore, it is possible to use the variational method for larger systems; considerable progress can be made using normal coordinates and an approximate form of Watson's kinetic-energy operator [10].

Here we stay with triatomic molecules. The next level of sophistication is to introduce the rotational angular momentum operator $\hat{J}$, enabling the calculation of rovibrational wavefunctions and the corresponding energy levels. The important advance here is that if a dipole surface is also available then the direct calculation of rovibrational transition probabilities is possible. Such calculations on H_2S, for example, have recently been reported [13]. The calculated intensities may be more reliable than observed values if good *ab initio* potentials and dipole surfaces are available. Of course, such calculations become more expensive, because the dimension of the variational matrix is $2J + 1$ time that of the corresponding $J = 0$ matrix.

When there is more than one electronic surface of interest, and vibrational levels may no longer be associated with one such surface, it is necessary to go beyond the Born–Oppenheimer approximation. The classic example is the Renner–Teller problem, typified by H_2O^+ and NH_2. Here the ground X^2B_1, and excited A^2A_1 surfaces are degenerate (Π_u) when the molecule is linear. We treated this problem some years ago [16] by extending the variational rovibrational method to make the expansion functions double in number, each being associated with both surfaces. The kinetic-energy operator in the Hamiltonian must have $\hat{J}$ replaced by $\hat{J} - \hat{L}$; this is most easily understood by recognising that the usual term '$B\hat{J}^2$' for the rotational kinetic energy of the nuclei must be replaced by '$B(J - L)^2$', the angular-momentum operator for the nuclei now being $\hat{J} - \hat{L}$. We studied CH_2^+; more recently H_2O^+ [17] and NH_2 [18] have also been studied.

However, the above cannot represent a complete treatment of such systems, especially for open-shell triatomic and electronically degenerate states. There are also observable splittings due to the coupling of all relevant angular momenta, including spin. Here we introduce spin by adding spin-expansion functions to the rovibronic expansion set. Likewise, in the kinetic-energy operator, $\hat{J}$ is replaced by $\hat{J} - \hat{L} - \hat{S}$. We must also introduce the spin–orbit effect, most simply through a term $AL \cdot S$. In this way it should be possible to reproduce all the observable effects in the rovibronic energy levels of these Renner–Teller molecules.

Following our earlier paper, we represent the Hamiltonian as

$$H = H_v + H_{VR}.$$

We use internal coordinates (R_1, R_2, θ). We denote by $\hat{J}$ the total-angular-momentum operator with respect to molecule-fixed axes, $\hat{L}$ the electronic-angular-momentum operator and $\hat{S}$ an effective spin-angular-momentum operator, both again defined with respect to molecule-fixed axes. In these axes the component angular-momenta operators of both $\hat{S}$ and $\hat{L}$ obey the standard commutation relations, while the component angular-momenta operators of $\hat{J}$ obey the non-standard commutation relations $[\hat{J}_x, \hat{J}_y] = -i\hat{J}_z$, but if we merely change the sign of $\hat{J}$, they obey the standard relations $[\hat{J}_x, \hat{J}_y] = i\hat{J}_z$. In effect, therefore, we replace $\hat{J} - \hat{L} - \hat{S}$ by $\hat{J} + \hat{L} + \hat{S}$ for the evaluation of matrix elements. A good discussion of this important aspect may be found in [19]. This is the notation we adopt. Following the method

of Handy [2], the parts of the Hamiltonian are thus

$$H_v(R_1, R_2, \theta) = -\frac{1}{4}\left(\frac{1}{\mu_1 R_1^2} + \frac{1}{\mu_2 R_2^2} - \frac{2\cos\theta}{mR_1 R_2}\right)\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta}\right)$$

$$-\frac{1}{4}\left(\frac{\partial^2}{\partial\theta^2} + \cot\theta\,\frac{\partial}{\partial\theta}\right)\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_1^2} - \frac{2\cos\theta}{mR_1 R_2}\right)$$

$$+\frac{1}{m}\left(\frac{1}{R_1}\frac{\partial}{\partial R_2} + \frac{1}{R_1}\frac{\partial}{\partial R_1}\right)\left(\sin\theta\,\frac{\partial}{\partial\theta} + \cos\theta\right)$$

$$-\frac{1}{2\mu}\frac{\partial^2}{\partial R_1^2} - \frac{1}{2\mu}\frac{\partial^2}{\partial R_2^2} - \frac{\cos\theta}{m}\frac{\partial^2}{\partial R_1 \partial R_2} + V, \qquad (1\,a)$$

$$H_{VR}(R_1, R_2, \theta, \hat{\mathbf{J}}, \hat{\mathbf{L}}, \hat{\mathbf{S}}) = \frac{1}{8\cos^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} + \frac{2}{mR_1 R_2}\right)(\hat{J}_z + \hat{L}_z + \hat{S}_z)^2$$

$$+\frac{1}{8\sin^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} - \frac{2}{mR_1 R_2}\right)(\hat{J}_x + \hat{L}_x + \hat{S}_x)^2$$

$$+\frac{1}{8}\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} + \frac{2\cos\theta}{mR_1 R_2}\right)(\hat{J}_y + \hat{L}_y + \hat{S}_y)^2$$

$$-\frac{1}{4\sin\theta}\left(\frac{1}{\mu R_1^2} - \frac{1}{\mu R_2^2}\right)[\hat{J}_z + \hat{L}_z + \hat{S}_z, \hat{J}_x + \hat{L}_x + \hat{S}_x]_+$$

$$+\frac{1}{2i}\left[\left(\frac{1}{\mu R_1^2} - \frac{1}{\mu R_2^2}\right)\left(\tfrac{1}{2}\cot\theta + \frac{\partial}{\partial\theta}\right)\right.$$

$$\left.+\frac{\sin\theta}{m}\left(\frac{1}{R_2}\frac{\partial}{\partial R_1} - \frac{1}{R_1}\frac{\partial}{\partial R_2}\right)\right](\hat{J}_y + \hat{L}_y + \hat{S}_y) + A\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}.$$

$$(1\,b)$$

Our choice of molecule-fixed axes has the molecule lying in the (x, z) plane, with Ox bisecting the $B_1 A B_2$ angle θ, and atom B_1 lying in the positive-(x, z) quadrant. m is the mass of atom A and μ is the reduced mass of AB. (Note that the $\pm$ signs were not clear in our previous paper [16]; indeed one of the great difficulties of this subject is the question of $\pm$ signs. We now have an independent verification of both our formula and computer program, having obtained results for $J \neq 0$ levels of a triatomic molecule identical with those obtained by Sutcliffe and Tennyson [14] using an entirely separate computer program. In the next section, for clarity, we give values for all relevant matrix elements of angular-momentum operators.)

We investigated the Renner–Teller effect in the H_2O^+ [17] and NH_2 [18] molecules using three-dimensional theoretical potential-energy functions. In those studies we used in the Renner–Teller Hamiltonian operator the *ab initio* three-dimensional functions of the expectation values of all necessary electronic-angular-momentum operators $\hat{\mathbf{L}}$, $\hat{\mathbf{L}}^2$ and $\hat{L}_i\hat{L}_j$. It was found that the approximation $\langle\hat{L}_z\rangle$, $\langle\hat{L}_z^2\rangle = 1$ (for Π states, neglecting $\hat{L}_x$, $\hat{L}_y$ etc.) worked very well, and that—in a reasonably good approximation—their geometry dependence can be neglected. This suggests that we may neglect the geometry dependence of the spin–orbit coupling. The main source of uncertainty in the Renner–Teller variational calculations remains the knowledge of the shape of the potential energy functions and the exact value for the barrier to linearity. This is because it crucially influences the position of the inter-

acting levels. In order to test the effects of the angular-momenta coupling, it is better to choose an example with no such barrier to linearity on the potential-energy functions.

One of the best experimentally investigated examples of such systems is the linear electronic ground state of CO_2^+ [20–22]. Both Renner–Teller components of the potential-energy functions have minima at the linear structure. The Renner–Teller coupling is basically determined by the splitting between both functions along the bending coordinate. In CO_2^+ the bending frequency is about $500\,cm^{-1}$, the Renner–Teller splittings lie in the range of $100\,cm^{-1}$ and the spin–orbit splittings in the range of $160\,cm^{-1}$. Hence the angular-momenta coupling effects are quite essential for the interpretation of the rovibronic energy-level patterns.

CO_2^+ has an anomalously low antisymmetric stretching frequency in the $\tilde{X}^2\Pi_g$ state when compared with neutral CO_2 or the $\tilde{A}^2\Pi_u$ state of CO_2^+ [21, 23, 24]. The spectroscopists explain this in terms of a 'vibronic coupling between the $\tilde{X}^2\Pi_g$ and $\tilde{A}^2\Pi_u$ states' (energy gap of about $27\,300\,cm^{-1}$). Such a discussion must apparently involve diabatic states. We prefer an explanation based on the adiabatic ground-state energy surface. We present in this work adiabatic three-dimensional potential-energy functions for the electronic ground state of CO_2^+ based on an *ab initio* MRCI computation [25] that reproduces the antisymmetric stretching fundamental frequency and its negative anharmonicity.

In other Renner–Teller molecules such as H_2O^+ or NH_2 the coupling of the nuclear-motion angular momenta, the electronic angular momenta and the electron spin starts to operate fully only for higher-lying rovibronic states close to and above the barrier to linearity on the corresponding potential-energy functions. The coupling of the electron-spin and nuclear-motion angular momenta is always present. It is the great advantage of our approach that all these couplings are automatically involved. The magnitude of the resulting effects depend only on the coupling strengths in a given spectral region. A study of gradual changes of the angular momenta coupling effects in H_2O^+ and NH_2 by this new variational technique will be published separately [26].

It is perhaps appropriate at this stage to compare our approach with important earlier work on Renner–Teller systems. Jungen and Merer [27] produced a series of papers on the Renner–Teller problem that references all earlier work. Their work used a Hamiltonian in the form (1), but they did not consider variations with R_1 and R_2, instead keeping these coordinates at their equilibrium values. The problem was reduced to a matrix diagonalisation involving the two one-dimensional surfaces in the bending coordinate, which were parametrised to give a representation of the spectrum. NH_2 and H_2O^+ were studied by Jungen and Merer, and, because their problem was essentially one-dimensional, they were able to study high rovibrational levels on both surfaces; within this framework a good understanding of the observed levels was achieved. Our approach is different, our kinetic-energy operator is almost exact and without semi-empirical parameters, and our potential-energy surfaces are *ab initio*. Our only parameter is the spin–orbit constant A, which should properly be replaced by a surface $A(R_1, R_2, \theta)$ to make the calculations complete.

In section 2 we give details of the expansion functions used in our procedure, together with additional information, which is new for this spin–rovibronic study. In section 3 we discuss our implementation of the method. The application to CO_2^+ is described in section 4.

2. Spin–rovibronic expansion functions

The kinetic-energy operator given in (1) is expressed in terms of angular-momentum operators $\hat{\boldsymbol{J}}$, $\hat{\boldsymbol{L}}$ and $\hat{\boldsymbol{S}}$. An angle γ may be defined as the projection of an angular-momentum operator M about the molecule-fixed z axis such that the eigenfunctions of $\hat{M}_z = -\mathrm{i}\,\partial/\partial\gamma$ have eigenvalues m. This definition therefore requires an eigenfunction of $\hat{M}_z$ to have the γ dependence $\mathrm{e}^{\mathrm{i}m\gamma}$, for which the following relationships apply:

$$\langle m \pm 1|\hat{M}_x|m\rangle = \tfrac{1}{2}[(M \mp m)(M \pm m + 1)]^{1/2},$$

$$\langle m \pm 1|\hat{M}_y|m\rangle = \mp\mathrm{i}\langle m \pm 1|\hat{M}_x|m\rangle,$$

$$\langle m|\hat{M}_z|m\rangle = m, \quad \langle m|\hat{M}_z^2|m\rangle = m^2,$$

$$\langle m|\hat{M}_x^2|m\rangle = \langle m|\hat{M}_y^2|m\rangle = \tfrac{1}{2}[M(M + 1) - m^2],$$

$$\langle m \pm 1|[\hat{M}_x, \hat{M}_z]_+|m\rangle = (m \pm \tfrac{1}{2})[(M \mp m)(M \pm m + 1)]^{1/2},$$

$$\langle m \pm 2|\hat{M}_x^2|m\rangle = \tfrac{1}{4}[(M \mp m + 1)(M \pm m + 2)(M \mp m)(M \pm m + 1)]^{1/2},$$

$$\langle m \pm 2|\hat{M}_y^2|m\rangle = -\langle m \pm 2|\hat{M}_x^2|m\rangle. \tag{2}$$

As in [16], we work with electronic wavefunctions $\Phi^\lambda(\gamma_e)$ that are combinations of the adiabatic (real) functions X and Y:

$$\Phi^{\pm\lambda}(\gamma_e) = \frac{1}{\sqrt{2}}(X \pm \mathrm{i}Y) \sim \mathrm{e}^{\pm\mathrm{i}\lambda\gamma_e}, \tag{3}$$

where λ is the eigenvalue of $\hat{L}_z$ when the molecule is linear.

In this paper, as in [16], we use only the constant (linear) values for the matrix elements of L_z and L_z^2, derived from (2) and (3):

$$\left.\begin{array}{l} \langle Y|\hat{L}_z|X\rangle = \mathrm{i}\lambda, \quad \langle X|\hat{L}_z|Y\rangle = -\mathrm{i}\lambda, \\ \langle X|\hat{L}_z^2|X\rangle = \langle Y|\hat{L}_z^2|Y\rangle = \lambda^2. \end{array}\right\} \tag{4}$$

H_2O^+, NH_2 are $^2\Pi_u$ electronic states and CO_2^+ is $^2\Pi_g$ for linear configurations. This means that we set $\lambda = 1$ in (4). Furthermore, we require spin eigenfunctions $\Phi^\sigma(\gamma_s) \sim \mathrm{e}^{\mathrm{i}\sigma\gamma_s}$ of S_z appropriate to the doublet electronic spin states. These we choose as $\alpha(\equiv \mathrm{e}^{\mathrm{i}\gamma_s/2})$ and $\beta(\equiv \mathrm{e}^{-\mathrm{i}\gamma_s/2})$, and we again assume that the expressions given in (2) are relevant to the entire surface. In particular,

$$\langle\alpha|\hat{S}_z|\alpha\rangle = \tfrac{1}{2}, \quad \langle\beta|\hat{S}_z|\beta\rangle = -\tfrac{1}{2} \tag{5}$$

define the spin eigenstates α and β respectively.

If k is the projection of the total angular momentum J along the molecule-fixed z axis, and l, λ and σ are the corresponding projections of the rotational, electronic and spin angular momenta, then

$$-J \leqslant k \leqslant J, \quad k = l + \lambda + \sigma. \tag{6}$$

We therefore suggest primitive basis functions for the linear angle-bend, electronic, spin and rotational motions [16] of the form:

$$\Psi_v^{Jk\lambda\sigma}(\theta, \alpha, \beta, \gamma, \gamma_r, \gamma_e, \gamma_s) = P_v^{|k-\lambda-\sigma|}(\cos\theta)\mathrm{e}^{\mathrm{i}(k-\lambda-\sigma)\gamma_r}D_{mk}^J(\alpha, \beta, \gamma)\Phi^\lambda(\gamma_e)\Phi^\sigma(\gamma_s), \tag{7}$$

Table 1. Symmetries of (a) spin–electronic functions $\phi^{\lambda,\sigma}$ (γ_e, γ_s) and (b) spin–vibronic functions $\phi^{k,\lambda,\sigma}$ (θ, γ_r, γ_e, γ_s).

(a)

| $e^{i\sigma\gamma_s}$ | $e^{i\lambda\gamma_e}$ | $\phi^{\lambda,\sigma}$ (γ_e, γ_s) | | |
σ	λ	$\omega = \lambda + \sigma$	Symmetry	Function
$+\frac{1}{2}$	$+1$	$+\frac{3}{2}$	Π_u	$e^{i\gamma_e}\alpha$
$-\frac{1}{2}$	-1	$-\frac{3}{2}$	Π_u	$e^{-i\gamma_e}\beta$
$-\frac{1}{2}$	$+1$	$+\frac{1}{2}$	Π_u	$e^{i\gamma_e}\beta$
$+\frac{1}{2}$	-1	$-\frac{1}{2}$	Π_u	$e^{-i\gamma_e}\alpha$

(b)

| $e^{i l \gamma_r}$ | | $\phi^{\lambda,\sigma}$ (γ_e, γ_s) | | $\phi^{k,\lambda,\sigma}$ (θ, γ_r, γ_e, γ_s) | | | |
l	Symmetry	ω	Symmetry	$k = l + \omega$	$n = l + \lambda$	Symmetry	Function
0	Σ_g^+	$\pm\frac{1}{2}$	Π_u	$\pm\frac{1}{2}$	± 1	Π_u	$P_v^0 e^{i\gamma_e}\beta$
–	–	$\pm\frac{3}{2}$	–	$\pm\frac{3}{2}$	± 1	Π_u	$P_v^0 e^{i\gamma_e}\alpha$
± 1	Π_u	$\pm\frac{1}{2}$	Π_u	$\pm\frac{3}{2}$	± 2	Δ_g	$P_v^1 e^{i\gamma_r} e^{i\gamma_e}\beta$
–	–	$\mp\frac{1}{2}$	–	$\pm\frac{1}{2}$	0	Σ_g^+	$P_v^1 e^{i\gamma_r} e^{-i\gamma_e}\alpha$
–	–	$\pm\frac{3}{2}$	–	$\pm\frac{5}{2}$	± 2	Δ_g	$P_v^1 e^{i\gamma_r} e^{i\gamma_e}\alpha$
–	–	$\mp\frac{3}{2}$	–	$\mp\frac{1}{2}$	0	$\Sigma^{\pm}$	$P_v^1 e^{-i\gamma_r} e^{i\gamma_e}\alpha$
± 2	Δ_g	$\pm\frac{1}{2}$	Π_u	$\pm\frac{5}{2}$	± 3	Φ_u	$P_v^2 e^{2i\gamma_r} e^{i\gamma_e}\beta$
–	–	$\mp\frac{1}{2}$	–	$\pm\frac{3}{2}$	± 1	Π_u	$P_v^2 e^{2i\gamma_r} e^{-i\gamma_e}\alpha$
–	–	$\pm\frac{3}{2}$	–	$\pm\frac{7}{2}$	± 3	Φ_u	$P_v^2 e^{2i\gamma_r} e^{i\gamma_e}\alpha$
–	–	$\mp\frac{3}{2}$	–	$\pm\frac{1}{2}$	± 1	Π_u	$P_v^2 e^{2i\gamma_r} e^{-i\gamma_e}\beta$

where $D^J_{mk}(\alpha, \beta, \gamma)$ and the $(2J + 1)$-degenerate $(-J \leqslant k \leqslant J)$ eigenfunctions of $\hat{J}_z$ with eigenvalues k are the elements of the rotation matrix

$$D^J_{mk}(\alpha, \beta, \gamma) = e^{ik\gamma} d^J_{mk}(\beta) e^{im\alpha}. \tag{8}$$

To complete the definitions, $P_v^{|l|}(\cos\theta) e^{il\gamma_r}$ ($l = k - \lambda - \sigma$) represents the basis function for the degenerate linear-angle bend, which can be described in terms of an associated Legendre function for the valence angle, $P_v^{|l|}(\cos\theta)$, and the function $e^{il\gamma_r}$ for rotation of the molecule about the linear axis.

In $D_{\infty h}$ the symmetries of the final spin–rovibronic wavefunctions must be labelled Σ_g^+, Σ_u^+, Σ_g^- and Σ_u^-. Note that these labels are isomorphic to the representation of the permutation–inversion group (PI) for this system, consisting of the identity E, the interchange of identical nuclei P, inversion of all coordinates in the origin $*$ and $(P*)$. Thus $+/-$ refers to even/odd under the interchange, and g/u refers to inversion.

Following arguments analogous to those presented in [16], we now discuss the possible combinations of the primitive basis functions $\Psi^{J,k,\lambda,\sigma}_\sigma$ in (7) that will lead to expansion functions with the above symmetries.

2.1. *Spin–electronic functions* $\Phi^\lambda(\gamma_e)\Phi^\sigma(\gamma_s)$

Because the total symmetry of the molecule is determined by the spatial part of the wavefunction, and therefore independent of spin, all spin–electronic functions are

determined solely by the symmetry of the electronic function $\Phi^{\lambda}(\gamma_e)$, and are therefore independent of $\Phi^{\sigma}(\gamma_s)$ In table 1 (*a*) we give explicit forms for the spin–electronic functions

$$\phi^{\lambda,\sigma}(\gamma_e, \gamma_s) = \phi^{\lambda}(\gamma_e)\phi^{\sigma}(\gamma_s) \sim e^{i\lambda\gamma_e}e^{i\sigma\gamma_s} \tag{9}$$

that arise for a $^2\Pi_u$ electronic state in terms of the quantum number $\omega = \lambda + \sigma$, appropriate to a $D_{\infty h}$ molecule. For the $^2\Pi_g$ electronic state (e.g. CO_2^+), g and u should be interchanged.

2.2. *Spin-vibronic functions* $P_v^{|l|}(\cos\theta)e^{il\gamma_r}\phi^{\lambda,\sigma}(\gamma_e, \gamma_s)$

The symmetry of the spin–vibronic function is determined by that of the linear-angle bend and that of the electronic wavefunction, as shown in table 1 (*b*). We denote the spin–vibronic functions $\Phi^{k,\lambda,\sigma}(\theta, \gamma_r, \gamma_e, \gamma_s)$ by the quantum numbers $k = l + \omega$ and $n = l + \lambda$. The former is the projection of the total angular momentum J along the molecule-fixed z axis, while the latter is the projection of $N = J - S$, and is therefore equal to the projection of the total spatial angular momentum about the molecule-fixed z axis, which determines the symmetry species. In table 1 (*b*) we give explicit forms of the spin–vibronic functions that lead to the symmetry species specified by n; we quote functions for positive n only (positive k):

$$\phi^{k,\lambda,\sigma}(\theta, \gamma_r, \gamma_e, \gamma_s) = P_v^{|l|}(\cos\theta)e^{il\gamma_r}\phi^{\lambda,\sigma}(\gamma_e, \gamma_s) \sim e^{il\gamma_r}e^{i\lambda\gamma_e}e^{i\sigma\gamma_s}. \tag{10}$$

2.3. *Spin-rovibronic functions* $\Phi^{k,\lambda,\sigma}(\theta, \gamma_r, \gamma_e, \gamma_s)D_{mk}^J(\alpha, \beta, \gamma)$

For a linear molecule there can be no component of rotational angular momentum about the linear axis, since all contributions must arise from orbital plus spin. Since the contribution to the total angular momentum arising from rotation of the molecule is represented by $l = k - \lambda - \sigma$, a contribution $e^{+il\gamma_r}$ must be exactly cancelled by the corresponding contribution $e^{-i(k-\lambda-\sigma)\gamma}$. For the values of $\pm k$ given in table 1 (*b*), therefore, the total-angular-momentum basis function must enter the final spin-rovibronic function with $e^{\pm ik\gamma}$. We can therefore simplify the form of (7) by taking γ_r as reference, to give

$$\Psi^{J,k,\lambda,\sigma}(\theta, \alpha, \beta, \gamma, \gamma_e, \gamma_s) = P_v^{|l|}(\cos\theta)D_{mk}^J(\alpha, \beta, \gamma)\Phi^{\lambda}(\gamma_e)\Phi^{\sigma}(\gamma_s) \tag{11}$$

for positive k. Because the functions $D_{mk}^J(\alpha, \beta, \gamma)$ are always symmetric to inversion (g) in a $D_{\infty h}$ molecule, the final basis functions (11) corresponding to $l = 0$ in table 1 (*b*) will be $\Sigma_u^\pm$, those corresponding to $l = \pm 1$ will be $\Sigma_g^\pm$, etc. All that remains is to determine the precise parity of the functions. We do this by first forming the correct linear combinations of $e^{i\lambda\gamma_e}e^{i\sigma\gamma_s}e^{ik\gamma}$ that transform as Σ in $D_{\infty h}$. For example, for the combination $l = 0$, $k = \pm\frac{1}{2}$ in table 1 (*b*) we take the $\Sigma_u^\pm$ pair

$$P_v^0 \frac{1}{\sqrt{2}} (e^{i\gamma_e}\beta D_{m-1/2}^J \pm e^{-i\gamma_e}\alpha D_{m1/2}^J). \tag{12}$$

We determine the parity of each of these combinations by the algorithm given by Zare [28]:

$$i_{SP}|n\lambda\rangle|v\rangle|S\sigma\rangle|Jkm\rangle = (-1)^{\lambda}(-1)^{S-\sigma}(-1)^{J-k}|n - \lambda\rangle|v\rangle|S - \sigma\rangle|J - km\rangle. \tag{13}$$

This leads to the following precise set of functions for $\lambda = 1, S = \frac{1}{2}, J = \frac{1}{2}$ ($k = \pm\frac{1}{2}$ in table 1 (b)):

$$
\left.
\begin{aligned}
&P_v^0 \frac{1}{\sqrt{2}} \left(e^{i\gamma_e} \beta D_{m-1/2}^{1/2} \pm e^{-i\gamma_e} \alpha D_{m1/2}^{1/2} \right), \quad \Sigma_u^\mp, \\[2mm]
&P_v^1 \frac{1}{\sqrt{2}} \left(e^{-i\gamma_e} \alpha D_{m-1/2}^{1/2} \pm e^{i\gamma_e} \beta D_{m1/2}^{1/2} \right), \quad \Sigma_g^\pm, \\[2mm]
&P_v^1 \frac{1}{\sqrt{2}} \left(e^{i\gamma_e} \alpha D_{m-1/2}^{1/2} \pm e^{-i\gamma_e} \beta D_{m1/2}^{1/2} \right), \quad \Sigma_g^\pm, \\[2mm]
&P_v^2 \frac{1}{\sqrt{2}} \left(e^{-i\gamma_e} \beta D_{m-1/2}^{1/2} \pm e^{i\gamma_e} \alpha D_{m1/2}^{1/2} \right), \quad \Sigma_u^\mp.
\end{aligned}
\right\}
\tag{14}
$$

We work with adiabatic potentials for X and Y, and so we have to convert (14) into real form, using (3). This leads to two sets of $\Sigma_u^\pm$ states whose only difference is a change in sign of the X and Y components, and similarly for $\Sigma_g^\pm$. We can therefore take the X and Y components separately as a basis for these symmetry species. We therefore take the following bend, spin, electronic and rotational functions for $J = \frac{1}{2}$:

$$
\left.
\begin{aligned}
&P_v^0 \frac{1}{\sqrt{2}} \left(X(\beta D_{m-1/2}^{1/2} + \alpha D_{m1/2}^{1/2}), \quad iY(\beta D_{m-1/2}^{1/2} - \alpha D_{m1/2}^{1/2}) \right), \quad \Sigma_u^-, \\[2mm]
&P_v^0 \frac{1}{\sqrt{2}} \left(X(\beta D_{m-1/2}^{1/2} - \alpha D_{m1/2}^{1/2}), \quad iY(\beta D_{m-1/2}^{1/2} + \alpha D_{m1/2}^{1/2}) \right), \quad \Sigma_u^+, \\[2mm]
&P_v^1 \frac{1}{\sqrt{2}} \left(X(\alpha D_{m-1/2}^{1/2} - \beta D_{m1/2}^{1/2}), \quad iY(\alpha D_{m-1/2}^{1/2} + \beta D_{m1/2}^{1/2}) \right), \quad \Sigma_g^-, \\[2mm]
&P_v^1 \frac{1}{\sqrt{2}} \left(X(\alpha D_{m-1/2}^{1/2} + \beta D_{m1/2}^{1/2}), \quad iY(\alpha D_{m-1/2}^{1/2} - \beta D_{m1/2}^{1/2}) \right), \quad \Sigma_g^+,
\end{aligned}
\right\}
\tag{15}
$$

where we have replaced P_v^2 by P_v^0. This is because the associated Legendre function $P_v^2(\cos\theta)$ can always be written in terms of $P_v^0(\cos\theta)$, as can all $P_v^l(\cos\phi)$ with even l. We therefore only work with $P_v^0(\cos\theta)$ and $P_v^1(\cos\theta)$ in this paper. The functions in (15) must now be coupled with the appropriate Σ_g^+ or Σ_u^+ stretching function $\Phi_v(R_1, R_2)$ (see next section) in order to form the complete basis function for $^2\Pi_u$ electronic states with $J = \frac{1}{2}$.

Similar functions arise for $J = \frac{3}{2}$. The $k = \pm\frac{1}{2}$ functions analogous to (15) change only by virtue of their parity. Hence we need only interchange '+' with '−' in (15) to arrive at the $J = \frac{3}{2}, k = \frac{1}{2}$ basis. The precise basis functions for $k = \frac{3}{2}$ are as follows:

$$
\left.
\begin{aligned}
&P_v^1 \frac{1}{\sqrt{2}} \left(X(\beta D_{m-3/2}^{3/2} + \alpha D_{m3/2}^{3/2}), \quad iY(\beta D_{m-3/2}^{3/2} - \alpha D_{m3/2}^{3/2}) \right), \quad \Sigma_g^-, \\[2mm]
&P_v^1 \frac{1}{\sqrt{2}} \left(X(\beta D_{m-3/2}^{3/2} - \alpha D_{m3/2}^{3/2}), \quad iY(\beta D_{m-3/2}^{3/2} + \alpha D_{m3/2}^{3/2}) \right), \quad \Sigma_g^+, \\[2mm]
&P_v^0 \frac{1}{\sqrt{2}} \left(X(\alpha D_{m-3/2}^{3/2} - \beta D_{m3/2}^{3/2}), \quad iY(\alpha D_{m-3/2}^{3/2} + \beta D_{m3/2}^{3/2}) \right), \quad \Sigma_u^+, \\[2mm]
&P_v^0 \frac{1}{\sqrt{2}} \left(X(\alpha D_{m-3/2}^{3/2} + \beta D_{m3/2}^{3/2}), \quad iY(\alpha D_{m-3/2}^{3/2} - \beta D_{m3/2}^{3/2}) \right), \quad \Sigma_u^-.
\end{aligned}
\right\}
\tag{16}
$$

Table 2. The symmetry of two-dimensional stretching functions Φ_v × spin–rovibronic expansion functions.

Symmetry in $D_{\infty h}$		Expansion function
$J = \tfrac{1}{2}$	$J = \tfrac{3}{2}$	
Σ_g^+	Σ_g^- : $\|l\|=1$, $\|k\|=\tfrac{1}{2}$	$\dfrac{1}{\sqrt{2}}\,\Phi_{v_1}(\Sigma_g^+)P_v^1 \times \begin{cases} X(\alpha D_{m-1/2}^J + \beta D_{m1/2}^J) \\ iY(\alpha D_{m-1/2}^J - \beta D_{m1/2}^J) \end{cases}$
	$\|l\|=0$	$\dfrac{1}{\sqrt{2}}\,\Phi_{v_2}(\Sigma_u^+)P_v^0 \times \begin{cases} X(\beta D_{m-1/2}^J - \alpha D_{m1/2}^J) \\ iY(\beta D_{m-1/2}^J + \alpha D_{m1/2}^J) \end{cases}$
	$\|l\|=1$, $\|k\|=\tfrac{3}{2}$	$\dfrac{1}{\sqrt{2}}\,\Phi_{v_1}(\Sigma_g^+)P_v^1 \times \begin{cases} X(\beta D_{m-3/2}^J + \alpha D_{m3/2}^J) \\ iY(\beta D_{m-1/2}^J - \alpha D_{m3/2}^J) \end{cases}$
	$\|l\|=0$	$\dfrac{1}{\sqrt{2}}\,\Phi_{v_2}(\Sigma_u^+)P_v^0 \times \begin{cases} X(\alpha D_{m-3/2}^J - \beta D_{m3/2}^J) \\ iY(\alpha D_{m-3/2}^J + \beta D_{m3/2}^J) \end{cases}$
Σ_u^+	Σ_u^-	Interchange $\Phi_{v_1}(\Sigma_g^+)$ and $\Phi_{v_2}(\Sigma_u^+)$
Σ_g^-	Σ_g^+	Interchange X and iY
Σ_u^-	Σ_u^+	$\begin{cases} \text{Interchange } \Phi_{v_1}(\Sigma_g^+) \text{ and } \Phi_{v_2}(\Sigma_u^+) \\ \text{Interchange } X \text{ and } iY \end{cases}$

To complete our derivation of the spin–rovibronic expansion functions, we present in table 2 the explicit forms of these functions for the four possible symmetries in $D_{\infty h}$ that result from products of two-dimensional stretching functions $\Phi_v(R_1, R_2)$ and the functions given in (14) and (15).

Finally, because the values of the matrix elements involving $D_{mk}^J(\alpha, \beta, \gamma)$ are independent of m in a field-free system, we choose to work with $m = \tfrac{1}{2}$ throughout.

3. Implementation of the variational method

Were it not for the fact that there is a practical limitation on the size of the spin–rovibronic matrix to be diagonalised, one could merely insert primitive basis functions of the form given in table 2 into the variational matrix determined by the Hamiltonian (1 *a*, *b*) and diagonalise. Unfortunately, to obtain converged energy levels by this method would require the diagonalisation of a dense matrix (even after the consideration of symmetry) of order 10^6 or more. What has to be done is to systematically contract the initial basis to form new expansion functions, starting with small subsets of the Hamiltonian and gradually tailoring the expansion functions for use in the complete Hamiltonian. This we do in five distinct stages.

3.1. *Two-dimensional stretch contraction*

Following an analysis suggested in [15], we choose to work with stretch basis functions $\phi_{n_1}(Q_1)$ and $\phi_{n_2}(Q_2)$ that are relevant to the symmetry-adapted

coordinates,

$$Q_1 = \frac{1}{\sqrt{2}} (R_1 + R_2), \left.\begin{array}{c} \\ \\ \\ \\ \end{array}\right\}$$

$$Q_2 = \frac{1}{\sqrt{2}} (R_1 - R_2), \qquad\qquad (17)$$

since, for molecules with twofold permutational symmetry, the coordinates Q_1 and Q_2 approximate to the normal modes of the molecule for small displacements from equilibrium. From the shapes of the effective one-dimensional potentials in Q_1 and Q_2, we concluded in [15] that Morse basis functions $\phi_{n_1}(Q_1)$ and harmonic-oscillator functions $\phi_{n_2}(Q_2)$ are optimum functions for use with these coordinates.

We carry out two analyses using these functions, the first involving only even quanta n_2 (describing Σ_g^+ stretching motions in $D_{\infty h}$) and the second involving only odd quanta n_2 (describing Σ_u^+ stretching motions). Furthermore, since it is expected that the stretching potentials are similar for the ground state and linear excited state (at their respective equilibria), we freeze the angle θ at that corresponding to the X electronic state (θ_e^X), and carry out two-dimensional diagonalisation using the expansion functions

$$\Phi_v(Q_1, Q_2) = \phi_{n_1}(Q_1)\phi_{n_2}(Q_2) \qquad\qquad (18)$$

in the effective Hamiltonian

$$H(R_1, R_2) = \hat{T}_v(R_1, R_2, \theta_e^X) + V_X(R_1, R_2, \theta_e^X), \qquad\qquad (19)$$

where T_v is the kinetic part of H_v, (1 a).

Because the primitive basis functions $\phi_{n_1}(Q_1)$ and $\phi_{n_2}(Q_2)$ are eigenfunctions of realistic effective Hamiltonians of the system, we follow our technique in [5] and carry out integrations over the potential $V_X(R_1, R_2, \theta_e^X)$ by use of the HEG [29] and Schwenke–Truhlar [30] method. All kinetic-energy integrals in R_1 and R_2 are evaluated by Gauss quadrature and stored for subsequent use. These diagonalisations lead to two sets of stretch expansion functions,

$$\Phi_{v_1}(\Sigma_g^+) = \sum_{n_1, n_2} C_{v_1}^{n_1, n_2} \phi_{n_1}(Q_1)\phi_{n_2}^{\text{even}}(Q_2), \left.\begin{array}{c} \\ \\ \\ \end{array}\right\}$$

$$\Phi_{v_2}(\Sigma_u^+) = \sum_{n_1, n_2} C_{V_2}^{n_1, n_2} \phi_{n_1}(Q_1)\phi_{n_2}^{\text{odd}}(Q_2), \qquad (20)$$

and these are the stretching expansion functions adopted in table 2. All kinetic- and potential-energy integrals involving these new functions can be evaluated from the $C_v^{n_1, n_2}$ and stored.

3.2. *One-dimensional bend contraction*

The pairs of expansion functions given in table 2 correspond to each of the adiabatic electronic states X and Y respectively. The primitive basis functions that we suggest ($P_v^0(\cos\theta)$ or $P_v^1(\cos\theta)$) are not eigenfunctions of a realistic effective one-dimensional Hamiltonian, and therefore many such functions are typically required. Furthermore, different subsets of these primitive functions are required for the equilibria of the X (bent or linear) and Y (linear) electronic states. We first of all form more suitable one-dimensional bending functions for each value of $|k| = \frac{1}{2}, \frac{3}{2}, \ldots, J$ for both $P_v^0(\cos\theta)$ and $P_v^1(\cos\theta)$ in table 2. This involves (for each k) two diagonalisations for $V_X(R_{1e}^X, R_{2e}^X, \theta)$ and two for $V_y(R_{1e}^X, R_{2e}^X, \theta)$, which are carried out at the

corresponding values of R_{1e}^X and R_{2e}^X using the effective Hamiltonian (we quote only that for the X electronic state):

$$
\hat{H}_X(\theta) = T_v(R_{1e}^X, R_{2e}^X, \theta) + V_X(R_{1e}^X, R_{2e}^X, \theta)
$$

$$
+ \frac{1}{8\cos^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_{1e}^2} + \frac{1}{\mu R_{2e}^2} + \frac{2}{mR_{1e}R_{2e}}\right)_X (\hat{J}_z^2 + \hat{L}_z^2 + \hat{S}_z^2 - 2\hat{J}_z\hat{S}_z)
$$

$$
+ \frac{1}{8\sin^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_{1e}^2} + \frac{1}{\mu R_{2e}^2} - \frac{2}{mR_{1e}R_{2e}}\right)_X (\hat{J}_x^2 + \hat{S}_x^2)
$$

$$
+ \frac{1}{8}\left(\frac{1}{\mu R_{1e}^2} + \frac{1}{\mu R_{2e}^2} + \frac{2\cos\theta}{mR_{1e}R_{2e}}\right)_X (\hat{J}_y^2 + \hat{S}_y^2). \tag{21}
$$

Note that only those components of $\hat{J}_x^2$ and $\hat{J}_y^2$ that are diagonal in k are used in (21). These diagonalisations lead to four sets of one-dimensional expansion functions for each value of k, the precise forms for $k = \frac{1}{2}$ (see table 2) being

$$
\Theta_{n_3}^{|l|}(X) = \frac{1}{\sqrt{2}}\sum_v c_v^{n_3}(X)P_v^l X(\alpha D_{1/2\,-1/2}^J + \beta D_{1/2\,1/2}^J),
$$

$$
\Theta_{n_3}^{|l|}(Y) = \frac{1}{\sqrt{2}}\sum_v c_v^{n_3}(Y)P_v^l iY(\alpha D_{1/2\,-1/2}^J - \beta D_{1/2\,1/2}^J),
$$

$$
\left.\begin{aligned}
\Theta_{n_3}^0(X) &= \frac{1}{\sqrt{2}}\sum_v d_v^{n_3}(X)P_v^0 X(\beta D_{1/2\,-1/2}^J - \alpha D_{1/2\,1/2}^J),
\end{aligned}\right\} \tag{22}
$$

$$
\Theta_{n_3}^0(Y) = \frac{1}{\sqrt{2}}\sum_v d_v^{n_3}(Y)P_v^0 iY(\beta D_{1/2\,-1/2}^J + \alpha D_{1/2\,1/2}^J).
$$

All integrals in this analysis are evaluated by Gauss quadrature, and we merely store the functions etc. at the corresponding Gauss integration points, originally occupied by $P_v^{|l|}$.

3.3. *Two-dimensional bend contractions*

Using subsets of the new one-dimensional bending expansion functions $\Theta_{n_3}^{|l|}(X)$ and $\Theta_{n_3}^{|l|}(Y)$ obtained above, we now form the final bending expansion functions, for use with the stretching functions $\Phi_v(R_1, R_2)$, by diagonalising two-dimensional X, Y matrices, again at R_{1e}^X and R_{2e}^X using the effective Hamiltonian.

$$
\hat{H}(\theta)^{X,Y} = \frac{1}{8\cos^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_{1e}^2} + \frac{1}{\mu R_{2e}^2} + \frac{2}{mR_{1e}R_{2e}}\right)2\hat{L}_z(\hat{J}_z + \hat{S}_z) + AL_zS_z. \tag{23}
$$

(Note the inclusion of the spin–orbit parameter A at this stage. We shall discuss the value chosen for this parameter in the later sections.)

Recall that (21) is still diagonal in k and σ, but is off-diagonal (through L_z) in the real electronic states X and Y. These diagonalisations therefore lead to two sets of bending expansion functions for each value of $|k|$, the precise forms for $|k| = \frac{1}{2}$ being

$$
\left.\begin{aligned}
\Theta_{v_3}^{|l|}(X, Y) &= \sum_{n_3} c_{n_3}^{v_3}(X)\Theta_{n_3}^{|l|}(X) + \sum_{n_3} c_{n_3}^{v_3}(Y)\Theta_{n_3}^{|l|}(Y), \\
\Theta_{v_3}^0(X, Y) &= \sum_{n_3} d_{n_3}^{v_3}(X)\Theta_{n_3}^0(X) + \sum_{n_3} d_{n_3}^{v_3}(Y)\Theta_{n_3}^0(Y).
\end{aligned}\right\} \tag{24}
$$

Again, the X and Y parts of these new functions are stored at the Gauss integration points, overwriting $\Theta_{n_3}^{|l|}(X)$ and $\Theta_{n_3}^{|l|}(Y)$ respectively.

3.4. *Three-dimensional k contraction*

The derivations of the bending expansion functions outlined in section 3.2 and 3.3 give rise to angular bases that are appropriate for each value of $|k| = \frac{1}{2}, \ldots, J$. We assume the optimised two-dimensional stretching expansion functions derived in section 3.1 to be appropriate for all values of $|k|$. Furthermore, the Hamiltonians used in the derivations of these functions (20), (22) and (24) contain the dominant terms in the complete Hamiltonian (1 *a, b*), and so it appears appropriate to treat the remaining terms as small perturbations and form three-dimensional expansion functions at this stage that are diagonal in the stretch symmetry and also in k, σ and $|l|$. We do this by setting up the Hamiltonian matrix for each of the stretching functions (20), in turn, with each of the optimised bending functions (24), in turn, a total of four for each value of $|k|$, and diagonalising the resulting matrices.

In this procedure we use the Hamiltonian

$$
\hat{H}_k(R_1, R_2, \theta) = \hat{T}_v(R_1, R_2, \theta) + V_X(R_1, R_2, \theta) + V_Y(R_1, R_2, \theta)
$$

$$
+ \frac{1}{8\cos^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} + \frac{2}{mR_1R_2}\right)
$$

$$
\times [\hat{J}_z^2 + \hat{L}_z^2 + \hat{S}_z^2 + 2(\hat{J}_z\hat{S}_z + \hat{J}_z\hat{L}_z + \hat{L}_z\hat{S}_z)]
$$

$$
+ \frac{1}{8\sin^2\frac{1}{2}\theta}\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} - \frac{2}{mR_1R_2}\right)(\hat{J}_x^2 + \hat{S}_x^2)
$$

$$
+ \frac{1}{8}\left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} + \frac{2\cos\theta}{mR_1R_2}\right)(\hat{J}_y^2 + \hat{S}_y^2) + A\hat{L}_z\hat{S}_z. \quad (25)
$$

The resulting expansion functions are now symmetry-adapted, according to which of the stretch functions (20) is used, the precise forms for $|k| = \frac{1}{2}$, $|l| = 1$ being

$$
\left.\begin{aligned}
\psi_v^{|l|}(\Sigma_g^+) &= \sum_{v_1}\sum_{v_3} C_{v_1,v_3}^v(\Sigma_g^+)\Phi_{v_1}(\Sigma_g^+)\Theta_{v_3}^{|l|}(X, Y), \\
\psi_v^{|l|}(\Sigma_u^+) &= \sum_{v_2}\sum_{v_3} C_{v_2,v_3}^v(\Sigma_u^+)\Phi_{v_2}(\Sigma_u^+)\Theta_{v_3}^{|l|}(X, Y).
\end{aligned}\right\} \quad (26)
$$

The coefficients of these eigenfunctions, C_{v_1,v_3}^v and C_{v_2,v_3}^v are stored, together with their eigenvalues, for each symmetry species (Σ_g^+ or Σ_u^+) and for each value of $|k|$ and $|l|$ (see table 2).

3.5. *Spin-rovibronic energy levels*

The remaining terms in the Hamiltonian, on completion of the procedure described in section 3.4, can be split into two parts. There are residual terms that are diagonal in k:

$$
\hat{T}_{kk}(R_1, R_2, \theta) = -\frac{1}{4\sin\theta}\left(\frac{1}{\mu R_1^2} - \frac{1}{\mu R_2^2}\right)[\hat{S}_x\hat{S}_z + \hat{S}_z\hat{S}_x + 2\hat{S}_x(\hat{L}_z + \hat{J}_z)]
$$

$$
+ \frac{1}{2i}\left[\left(\frac{1}{\mu R_1^2} - \frac{1}{\mu R_2^2}\right)\left(\frac{1}{2}\cot\theta + \frac{\partial}{\partial\theta}\right) + \frac{\sin\theta}{m}\left(\frac{1}{R_2}\frac{\partial}{\partial R_1} - \frac{1}{R_1}\frac{\partial}{\partial R_2}\right)\right]\hat{S}_y.
$$

$$
(27)
$$

The remaining terms are all off-diagonal in k:

$$\hat{T}_{kk'}(R_1, R_2, \theta) = \frac{1}{8 \sin^2 \frac{1}{2}\theta} \left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} - \frac{2}{mR_1 R_2} \right) (\hat{J}_x^2 + 2\hat{J}_x \hat{S}_x)$$

$$+ \frac{1}{8} \left(\frac{1}{\mu R_1^2} + \frac{1}{\mu R_2^2} + \frac{2 \cos \theta}{mR_1 R_2} \right) (\hat{J}_y^2 + 2\hat{J}_y \hat{S}_y)$$

$$- \frac{1}{4 \sin \theta} \left(\frac{1}{\mu R_1^2} - \frac{1}{\mu R_2^2} \right) (\hat{J}_x \hat{J}_z + \hat{J}_z \hat{J}_x + 2\hat{J}_x (\hat{L}_z + \hat{S}_z))$$

$$+ \frac{1}{2i} \left[\left(\frac{1}{\mu R_1^2} - \frac{1}{\mu R_2^2} \right) \left(\frac{1}{2}\cot \theta + \frac{\partial}{\partial \theta} \right) \right.$$

$$\left. + \frac{\sin \theta}{m} \left(\frac{1}{R_2} \frac{\partial}{\partial R_1} - \frac{1}{R_1} \frac{\partial}{\partial R_2} \right) \right] \hat{J}_y. \qquad (28)$$

The k-diagonal kinetic-energy operator $T_{kk}(R_1, R_2, \theta)$ consists of two components. The first mixes levels of different stretch symmetry and opposing spins for the *same* electronic state X or Y, while the second mixes corresponding levels of *different* electronic states X and Y.

The second term, off-diagonal in k, $T_{kk'}$, consists of three such contributions. The first is merely the standard $\Delta k = \pm 1, \pm 2$ term for levels of the *same* electronic state and aligned spins. The second term mixes $\Delta k = \pm 1$ levels of the *same* electronic state but with opposing spins. Note that there is no term in the complete Hamiltonian that can mix $\Delta k \neq 0$ levels of different electronic states with opposing spins.

In practice, we treat terms (27) and (28) together by first placing the eigenvalues from the procedure of section 3.4 on the diagonal of the complete Hamiltonian matrix for each of the spin–rovibronic symmetries in turn, using blocks of functions specified in table 2. The number of functions for each value of $|k|$ and $|l|$ are selected by an energy criterion when storing eigenvalues in the procedure in section 3.4.

4. Application to the electronic ground state of CO_2^+ ($\tilde{X}^2\Pi_g$)

We have performed [25] very large scale multireference configuration-interaction (MRCI) calculations for CO_2^+. The details of the *ab initio* calculations will be published separately: a large 13s 8p basis set with two sets of d functions and one set of f functions were used for each atom. The MRCI calculations were all single and double excitations from 29 reference configurations, which were selected from a complete active-space self-consistent field (CASSCF) calculation. All valence electrons were correlated. The equilibrium geometry was determined to be $D_{\infty h}$, with $R_{CO} = 2 \cdot 2207$ bohr.

The energies of both components ($^2A_1^{42}A^1$) of the Renner–Teller problem were calculated, using this MRCI method, at 53 points near the equilibrium geometry, sampling all three dimensions. We believe that these were sufficient for a representation of these three-dimensional surfaces in this region. These energies were then fitted to polynomial functions of the form

$$V(R_1, R_2, \theta) = \sum_{i,j,k} c_{ijk} R_1^i R_2^j \theta^k, \qquad (29)$$

The expansion functions R_1 and R_2 have the Morse form [31]

$$R_i = \beta^{-1} \left\{ 1 - \exp\left[-\beta \left(\frac{r}{r_0} - 1 \right) \right] \right\}, \quad \beta = \left(\frac{f_{rr}}{D_e} \right)^{1/2}. \qquad (30)$$

Table 3. Vibronic energies (in cm^{-1}) for the lowest few states of $\tilde{X}\,^2\Pi\ CO_2^+$.

State	Observed energy[a]	This work	MRCI[b]
$(000)\,^2\Pi_{1/2}$	159·598	158·9	158·9
$(010)\,^2\Sigma^+$	467·259	473·6	533·2
$(010)\,^2\Sigma^-$	719·174	727·6	760·5
$(010)\,^2\Delta_{5/2}$	511·599	511·2	563·1
$(010)\,^2\Delta_{3/2}$	668·040	667·9	720·1
$(020)\,^2\Phi_{7/2}$	1021·000	1016·9	1120·9
$(020)\,^2\Phi_{5/2}$	1173·052	1171·3	1275·4
$(020)\,\mu\,^2\Pi_{3/2}$	939·684	942·2	1050·4
$(020)\,\mu\,^2\Pi_{1/2}$	949·995	957·6	1068·2
$(100)\,^2\Pi_{3/2}$	1242·023	1242·5	1282·0
$(020)\,\kappa\,^2\Pi_{1/2}$	1250·606	1258·7	1323·1
$(020)\,\kappa\,^2\Pi_{3/2}$	1287·489	1297·1	1275·4
$(100)\,^2\Pi_{1/2}$	1425·153	1423·6	1457·6
$(001)\,^2\Pi_{3/2}$	1423·0[b]	1435·4	1494·4
$(001)\,^2\Pi_{1/2}$	1581·66[c]	1594·6	1653·2
$(002)\,^2\Pi_{3/2}$	2938·8	2923·1	3020·7
$(002)\,^2\Pi_{1/2}$	3096·2	3082·7	3179·6

[a] Referenced to the $(000)\,^2\Pi_{3/2}$ spin–orbit component. The 'observed' energies are the hypothetical vibronic energies calculated from the fit to the vibrational–rotational lines and combination differences followed by setting all J-dependent parameters equal to zero (cf. [20, 22]).
[b] From [25].
[c] From [21].

The angle θ is the displacement from 180°. Symmetry demands that $c_{ijk} = c_{jik}$. r_0 is the equilibrium value of the bond length r Both components of the surface must have a common two-dimensional potential-energy function for $\theta = 180°$. In all our representation of the surfaces this is fulfilled to within less than 1 cm^{-1} for their low-energy parts.

To obtain a good fit to the *ab initio* points using the form (29), it was necessary to include terms up to R_1^6, R_2^6 and θ^4, using 32 parameters c_{ijk} in total. The fits were such that the maximum error was 6×10^{-5} hartree (15 cm^{-1}).

Using these MRCI generated surfaces, and a spin–orbit parameter $A = -160$ cm^{-1} taken from [20], [22], the vibronic energies given in the final column of table 3 were obtained. These should be compared with the observed energies in the second column. It will be seen that the (010) bending frequencies are too high by approximately 50 cm^{-1}, the (100) stretch frequencies by 30 cm^{-1} and the (001) antisymmetric stretch frequencies by 70 cm^{-1} (the probable reason for this is a lack of higher-order dynamical correlation effects). The most significant result from these MRCI calculations, however, concern the values of $1\nu_3$ $(= 1494$ cm$^{-1})$ and $2\nu_3 - 1\nu_3$ $(= 1526$ cm$^{-1})$. In other words, these *ab initio* calculations have clearly shown an anomalously low value for $1\nu_3$ and also shown a negative anharmonicity for the antisymmetric stretch vibration of CO_2^+. This agrees with the experimental situation where $1\nu_3 = 1423$ cm^{-1} and $2\nu_3 - 1\nu_3 = 1515$ cm^{-1}. (For CO_2, $1\nu_3 = 2349$ cm^{-1}). The current explanation of this experimentally observed effect is in terms of a vibronic interaction between the 'diabatic' $\tilde{X}\,^2\Pi_g$ and $\tilde{A}\,^2\Pi_u$ electronic states of CO_2^+, however such diabatic states may

be defined. This seems rather unclear when it is noted that the $^2\Pi_u$ surface is $27\,300\,\text{cm}^{-1}$ above the $^2\Pi_g$ surface. The better explanation, arising from our MRCI results in table 3, is in terms of electronic structure theory and adiabatic surfaces. There will be a tendency for CO_2^+ to have an asymmetric equilibrium geometry (arising from the interaction of valence-bond configurations :Ö=C=Ö: with configurations :Ö–C≡O: . In fact, a $D_{\infty h}$ equilibrium geometry is found, but the effects of configuration inter-action must make the surface very flat in the direction of antisymmetric stretch displacements. Indeed, it is found that the coefficient in a normal-coordinate expan-sion of this potential is large and positive. Such a flat surface leads to a negative anharmonicity, as may be realised by considering the limit of a square-well potential. In our view, based on these calculations, both the low value of $1\nu_3$ and the negative anharmonicity must arise naturally from good *ab initio* quantum-chemical calcu-lations on the adiabatic $^2\Pi$ surface. CO_2^+ is not an easy system on which to perform good calculations; we encountered severe difficulties in some preliminary calculations using the restricted Hartree–Fock method arising from charge-transfer effects leading to instabilities. Similar difficulties arose in CEPA calculations based on the Hartree–Fock reference. Earlier studies demonstrate the difficulty: for example, Praet *et al.* [32] calculated a bent $^2B_2$ structure ($\theta_e = 172°$), and Grimm and Larsson [33] a symmetric linear structure. An analysis of calculations for the infrared intensities of CO_2^+ given by Chin and Person [34] (showing a hundred-fold decrease for the ν_3 mode compared with CO_2), indicated the importance of other ionic configurations.

There is a similar history of the study of the isoelectronic molecule BO_2. Kawaguchi *et al.* [24] invoked a similar 'diabatic' argument involving the $\tilde{X}\,^2\Pi_g$ and $\tilde{A}\,^2\Pi_u$ states to explain away the negative anharmonicity. Indeed, the result of their analysis suggested that the ground state of the molecule could have a double-minimum potential along the antisymmetric-displacement coordinate. Electronic-structure cal-culations [35] on the $\tilde{X}\,^2\Pi_g$ state predict a $D_{\infty h}$ structure. We suggest that the negative anharmonicity of the ν_3 mode of $^2\Pi_g$ BO_2 will again be explained by good MRCI calculations on this ground-state adiabatic surface at geometries near to equilibrium.

Because of the difference between the MRCI values for the fundamental frequen-cies and the experimental values, as seen in table 3, we have modified the MRCI potentials to reproduce the known data more accurately. A compact representation for both these new potentials is given in table 4; these were derived from a fit to the *ab initio* points, followed by an adjustment to c_{200}, c_{110}, c_{002} and c_{310}. The resulting energies are given in the third column of table 3. The observed vibronic energies in this table are derived from the rovibronic transition energies of Larcher *et al.* [20] (ν_1, ν_2), Frye and Sears [22] (ν_2) and Kawagachi *et al.* [21] (ν_3). The agreement between the observed vibronic energies and our calculated values using the modified potentials is very good. We therefore believe that these potentials are good representations of the potential surfaces in the region of the equilibrium geometry.

The energy levels that we obtain contain all the spectroscopic features. Herzberg [36] discusses in detail the expected features of the energy levels of Renner–Teller systems, but his and other [37, 38] analyses are based on model Hamiltonians (e.g. Renner–Teller parameters or spin-splitting parameters). Our levels arise from a variational study with an almost *ab initio* Hamiltonian.

The vibronic levels of an electronically degenerate open shell state of a triatomic molecule are usually classified [35] according to $K = \Lambda + 1$ (in our notation *n*; cf. table 1) and $P = \Lambda + 1 + \Sigma$ (in our notation *k*; cf. table 1), the projections of the

Table 4. Expansion coefficients[a] (in au) of the three-dimensional near-equilibrium potential-energy functions of the $\tilde{X}\,^2\Pi_g$ state of CO_2^+.

Lower component[b]:						
	c_{000}	-187.806989	c_{200}	1.627690	c_{110}	1.620000
	c_{002}	0.044021	c_{300}	-4.192503	c_{210}	-0.133088
	c_{102}	-0.0574514	c_{400}	4.477955	c_{310}	-10.000000
	c_{220}	9.077020	c_{202}	0.418846	c_{112}	-0.541547
	c_{004}	-0.000733				
Upper component[c]:						
	c_{000}	-187.806990	c_{200}	1.627690	c_{110}	1.620000
	c_{002}	0.065756	c_{300}	-4.191787	c_{210}	-0.132690
	c_{102}	-0.100147	c_{400}	4.476140	c_{310}	-10.000000
	c_{220}	9.074054	c_{202}	0.329212	c_{112}	-0.174062
	c_{004}	0.005381				

[a] Note that $c_{ijk} = c_{jik}$.
[b] $R_1^{\mathrm{ref}} = R_2^{\mathrm{ref}} = 2.220702$ au, $\theta^{\mathrm{ref}} = 180°$; $f_{\mathrm{rr}} = 12\,\mathrm{aJ\,\mathring{A}^{-1}}$, $D_e = 8\,\mathrm{eV}$.
[c] $R_1^{\mathrm{ref}} = R_2^{\mathrm{ref}} = 2.220713$ au, $\theta^{\mathrm{ref}} = 180°$; $f_{\mathrm{rr}} = 12\,\mathrm{aJ\,\mathring{A}^{-1}}$, $D_e = 8\,\mathrm{eV}$.

angular momenta along the linear axis. For the $^2\Pi$ state $\Lambda = \pm 1$, $\Sigma = \pm\frac{1}{2}$ and l_i can take the values v_i, $v_i - 2, \ldots, -v_i$, where v_i is the quantum number of the linear-angle bend. The symmetry symbols Σ, Π and Δ in table 3 correspond to $K = 0$, 1, 2, 3. The upper index relates the vibronic levels to an electronic doublet state, the lower index corresponds to P. For $K > 0$ the pattern begins with 'unique levels' split only in P. For higher quanta in v_2 the vibronic bending levels split into μ and κ levels (lower and upper components) due to Renner–Teller coupling. Similar patterns exist also in the v_2 combination bands, the pure stretching levels are split by spin–orbit coupling. Each of these levels has its own stack of rovibronic states. In these states, additional splittings due to K-doubling can occur. K-doubling in Renner–Teller systems can be understood as a superposition of Λ- and l-doubling. The Λ-doubling contribution resulting from an interaction between Π and Σ electronic states is not considered in the present Hamiltonian, which acts only in the space of the $^2\Pi_g$ state of CO_2^+. This contribution depends on B_e^2/T_e (B_e is the rotational constant and T_e the $B^2\Sigma_u^+ - X^2\Pi_g$ transition energy in CO_2^+), whereas the l-doubling contribution has the magnitude B_e^2/ω_e (ω_2 is the bending frequency in the $X^2\Pi_g$ state). Hence to a good approximation the K-doubling effect can also be reproduced already within the present approach.

The experimental spectra [22] have been investigated in the region of highly excited rotational levels ($J \approx 41/2$) and therefore the positions of the rovibronic levels are not directly comparable with our results for low J values. We have used [25] the rotational constants derived from the analysis of the spectral data [22] and calculated the rovibronic levels for low J values for Hund's coupling cases a and b. Our variational results turned out to be in excellent agreement with such extrapolated experimental energies, the deviations amount to about $0.01\,\mathrm{cm}^{-1}$. Also our K-doubling energy differences [25] in the Π vibronic states agree to within 10% with the experimental values [22].

We believe that our analysis leads to a deeper understanding of the origins and magnitude of the various rotational stacks, and the associated splittings and separations. By examining the effects of each of the terms in $(\hat{J} - \hat{L} - \hat{S})^2$ that arise in the kinetic-energy operator, as well as the spin–orbit operator $A\hat{L} \cdot \hat{S}$,

we are in a strong position to do this. This topic will form the basis of a subsequent paper.

Finally, therefore, in this section we observe that we have obtained potentials for both Renner–Teller surfaces that closely reproduce the rovibronic levels, as seen in table 3. For example, it has been known that the v_1 and $2v_2$ bands show a Fermi resonance [20, 22], our levels for $2v_1$ and $1v_1$ agree to within $10\,\text{cm}^{-1}$ with the levels deduced from experiment. The experimental [21] v_3 transition frequency has been reproduced to within $12\,\text{cm}^{-1}$, and the reversed anharmonicity to within $28\,\text{cm}^{-1}$.

These potential-energy functions for the two Renner–Teller components of the $\tilde{X}\,^2\Pi_g$ state of CO_2^+ represent the first analytical three-dimensional functions of this type. If some more experimental rovibronic levels become available, our functions can be employed as a basis for a more accurate compact characterisation of the CO_2^+ ion.

5. Conclusion

In this paper we have used the variational method for the study of the rovibrational energy levels of triatomic molecules, including the following effects:

(a) two potential-energy surfaces X and Y that interact through the electronic-angular-momentum operator $\hat{L}$;

(b) the electronic spin of the surfaces and relevant matrix elements of the spin angular momentum of the odd electron $\hat{S}$;

(c) a treatment of spin–rotation, orbital–rotation and spin–orbit interactions using the effective angular-momentum operator $\hat{J} - \hat{L} - \hat{S}$ and the spin-orbit term $A\hat{L} \cdot \hat{S}$, all simultaneously.

In our study of CO_2^+ all of these are important, and it has been seen how the results of our calculations have reproduced the experimental patterns. In later papers we shall study H_2O^+ and NH_2, where the couplings referred to above will have different effects at different energies. For example, near the bottom of the X state, the rovibrational levels will be split by spin–rotation coupling $\hat{N} \cdot \hat{S}$, but near the linear geometry the Coriolis term $\hat{J} \cdot \hat{L}$ is responsible for the principal Renner–Teller effect, and the spin–orbit interaction $\hat{L} \cdot \hat{S}$ also has a much greater effect in this region. In summary, we should be in a position to provide a complete understanding of the rovibronic spectrum.

References

[1] WATSON, J. K. G., 1968, *Molec. Phys.*, **15**, 479.
[2] HANDY, N. C., 1987, *Molec. Phys.*, **61**, 207.
[3] CARNEY, G. D., SPRANDEL, L. L., and KERN, C. W., 1978, *Adv. chem. Phys.*, **37**, 205.
[4] WHITEHEAD, R. J., and HANDY, N. C., 1975, *J. molec. Spectrosc.*, **55**, 356.
[5] CARTER, S., and HANDY, N. C., 1986, *Molec. Phys.*, **57**, 175.
[6] MILLER, S., and TENNYSON, J., 1987, *J. molec. Spectrosc.*, **128**, 183.
[7] BACIC, Z., and LIGHT, J. C., 1986, *J. chem. Phys.*, **85**, 4594.
[8] MAESSEN, B., and WOLFSBERG, M., 1986, *J. chem. Phys.*, **80**, 4651.
[9] BOWMAN, J. M., BITTMAN, J. S., and HARDING, L. B., 1986, *J. chem. Phys.*, **85**, 911.

[10] ROMANOWSKI, H., BOWMAN, J. M. , and HARDING, L. B., 1985, *J. chem. Phys.*, **82,** 4155.
[11] WILLETTS, A., GAW, J. F., HANDY, N. C., and CARTER, S., 1989, *J. molec. Spectrosc.*, **135,** 370.
[12] MILLER, S., TENNYSON, J., and SUTCLIFFE, B. T., 1989, *Molec. Phys.*, **66,** 429.
[13] SENEKOWITSCH, J., CARTER, S., ZILCH, A., WERNER, H.-J., HANDY, N. C., and ROSMUS, P., 1989, *J. chem. Phys.*, **90,** 783.
[14] CARTER, S., ROSMUS, P., HANDY, N. C., MILLER, S., TENNYSON, J., and SUTCLIFFE, B. J., 1989, *Comput. Phys. Commun.*, **55,** 71.
[15] CARTER, S., HANDY, N. C., and MILLS, I. M., 1990, *Phil. Trans. R. Soc. Lond.* A, in press.
[16] CARTER, S., and HANDY, N. C., 1986, *Molec. Phys.*, **52,** 1367.
[17] WEISS, B., CARTER, S., HANDY, N. C., KNOWLES, P. J., WERNER, H.-J., and ROSMUS, P. (to be published).
[18] MANZ, U., CARTER, S., HANDY, N. C., KNOWLES, P. J., WERNER, H.-J., and ROSMUS, P. (to be published).
[19] BROWN, J. M., and HOWARD, B. J., 1976, *Molec. Phys.*, **31,** 1517.
[20] LARCHER, C., GAUYACQ, D., and ROSTAS, J., 1980, *J. Chim. phys.*, **77,** 656.
[21] KAWAGUCHI, K., YAMADA, C., and HIROTA, E., 1985, *J. chem. Phys.*, **82,** 1174.
[22] FRYE, J. M., and SEARS, T., 1987, *Molec. Phys.*, **62,** 919.
[23] GAUYACQ, D., and JUNGEN, C., 1980, *Molec. Phys.*, **41,** 383.
[24] KAWAGUCHI, K., HIROTA, E., and YAMADA, C., 1981, *Molec. Phys.*, **44,** 509.
[25] CHAMBAUD, G., SPIELFIELD, A., FEAUTRIER, N., BROMMER, M., and ROSMUS, P., 1990, *J. chem. Phys.* (submitted).
[26] CARTER, S., HANDY, N. C., CHAMBAUD, G., and ROSMUS, P. (to be published).
[27] JUNGEN, C., and MERER, A. J., 1980, *Molec. Phys.*, **40,** 1, 25, 65 and 95.
[28] ZARE, R. N., 1988, *Angular Momentum* (Wiley).
[29] HARRIS, D. O., ENGERHOLME, C. O., and GWINN, W., 1965, *J. chem. Phys.*, **43,** 1515.
[30] SCHWENKE, D. W., and TRUHLAR, D. G., 1984, *Comput. Phys. Commun.*, **34,** 57.
[31] MEYER, W., BOTSCHWINA, P., and BURTON, P., 1986, *J. chem. Phys.*, **84,** 891.
[32] PRAET, M. T., LORQUET, J. C., and RASEER, G., 1982, *J. chem. Phys.*, **77,** 4611.
[33] GRIMM, F. A., and LARSSON, M., 1984, *Physica scripta*, **29,** 337.
[34] CHIN, S., and PERSON, W. B., 1984, *J. phys. Chem.*, **88,** 553.
[35] NGUYEN, M. T., 1986, *Molec. Phys.*, **58,** 655.
[36] HERZBERG, G., 1966, *Electronic Structure of Polyatomic Molecules* (Van Nostrand).
[37] HOUGEN, J. T., 1962, *J. chem. Phys.*, **36,** 519.
[38] BROWN, J. M., and JØRGENSEN, F., 1982, *Molec. Phys.*, **47,** 1065.