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THE ELECTRONIC SPECTRA AND ENERGY LEVELS OF TRIATOMIC MOLECULES

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Résumé. — On discute les modèles théoriques employés pour l'interprétation des spectres électroniques de molécules triatomiques. Il est possible qu'une molécule pliée est un rotateur fortement asymétrique. Les molécules linéaires peuvent montrer le couplage vibronique des moments cinétiques électronique et vibrationnel, et le couplage spin-orbite. Pour molécules pliées des types XH_2 et HXY une large amplitude de vibration de déformation angulaire peut aboutir à quelques effets caractéristiques tant des molécules pliées que des molécules linéaires. On présente des calculs propres de l'état $\tilde{A}, {}^2A_1$ de PH_2 .

Abstract. — A discussion is given of the theoretical models which have been used for the interpretation of the electronic spectra of triatomic molecules. Bent molecules may be strongly asymmetric rotors. Linear molecules may exhibit vibronic coupling between electronic and vibrational angular momentum and spin-orbit coupling. In bent molecules of the types XH_2 and HXY a large amplitude of the bending vibration may lead to some of the effects characteristic of both bent molecules and of linear molecules. Model calculations are presented for the $\tilde{A}, {}^2A_1$ state of PH_2 .

The electronic spectra of triatomic molecules show a wide variety of fine structures and of energy level patterns. Linear triatomic molecules may exhibit any of the characteristics of diatomic molecules, such as the multiplet splittings arising from the possession of electronic and spin angular momentum, plus the additional interactions arising from the presence of a non-totally symmetric bending vibration with its associated angular momentum. Strongly bent molecules cannot have orbital degeneracy, and thus some of the characteristic coupling cases of linear molecules are not possible, but they may be strongly asymmetric top rotors. There is also a class of molecules which is intermediate between these two types, having some of the characteristics of both linear and bent molecules.

This paper will review these various types of behaviour with particular emphasis on the intermediate types. The various stages in the analysis of the electronic spectrum of a polyatomic molecule may be summarised as :

- i) The characterisation of the molecular point group and the species of the electronic wavefunction in all known states ;
- ii) The assignment of quantum numbers to all transitions ;
- iii) The determination of an equilibrium — or zero level — geometrical structure and vibration frequencies ;
- iv) The deduction of a model which can represent all the term values and line intensities, that is, the construction of a suitable effective Hamiltonian from the complete molecular Hamiltonian.

v) The correlation of the observed electronic states and spectroscopic constants in terms of electronic theories.

The difficulty with the molecules of intermediate behaviour arises particularly at stage (iv). Spectroscopic models are based on the use of perturbation theory, and it is not always possible to separate the degrees of freedom in the zero approximation sufficiently to give a suitable expansion for the Hamiltonian. In some cases the analysis of a set of energy levels may therefore be more qualitative than quantitative, and may rely on empirical models. For these reasons it will be appropriate to discuss the limiting cases first.

Bent Molecules. — A bent triatomic molecule in a singlet state possess no internal angular momentum, and in the absence of perturbations the rotational levels of each vibronic state should be well represented by the non-rigid asymmetric top Hamiltonian :

$$\mathcal{H}_r = AN_a^2 + BN_b^2 + CN_c^2 + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} N_\alpha N_\beta N_\gamma N_\delta \dots ;$$

$$(\alpha, \beta, \gamma, \delta = a, b, c). \quad (1)$$

The centrifugal distortion may alternatively be expressed in terms of the constants D_J, D_{JK}, D_K , etc. appropriate to one of the limiting symmetric top representations. The absorption and emission spectrum of HNO [1], [2], [3] is a very good example of a well-behaved transition between two bent states. The A rotational constant is much larger than B and C in both

states (Table I) because of the light mass of the hydrogen atom. Consequently the sub-bands of various K_a in each vibronic band are well separated and the fine structure is completely resolved, even close to the band centre. The sub-band structure and the «missing lines» in the observed branches show that the transition is a perpendicular transition ($\Delta K_a = \pm 1$) of a near symmetric top. For low values of K_a the rotational levels of both states show substantial asymmetric top splittings, and the observed branches indicate that the band obeys type-C selection rules. The electronic transition is thus ${}^1A''-{}^1A'$.

For heavier molecules it is not always possible to achieve a complete resolution of the rotational structure, and a complete analysis cannot therefore be based entirely on line assignments. Figure 1b shows a

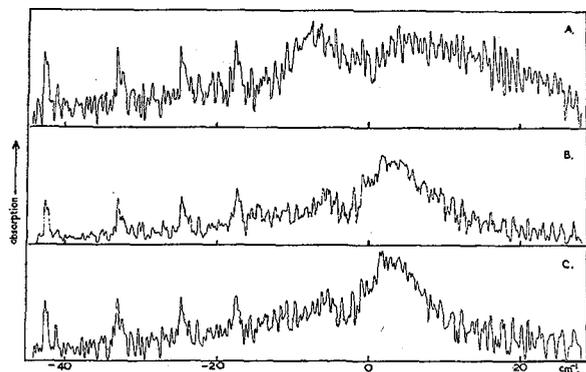


FIG. 1. — Rotational contour of part of the 25805 cm^{-1} ($0, 0, 1-0, 0, 0$) band of the $\tilde{A}-\tilde{X}$ system of NSF at -78°C .

- Simulated type-B band contour.
- Experimental microdensitometer trace.
- Simulated type-C band contour.

microphotometer tracing of the centre of an absorption band of NSF which has recently been obtained in my laboratory [4]. The wings of this band show well resolved sub-bands corresponding to $\Delta K_a = \pm 1$, but at sufficiently high values of K_a that there are no asymmetry splittings. Calculations based on provisional rotational constants showed that the only branches for which both the upper and lower state rotational asymmetry splittings would be significant lie close to the band centre, where the density of lines is so great that the average separation between neighbouring lines is comparable with the Doppler width of individual lines. It is therefore impossible to distinguish unambiguously between a type-B and a type-C band on the basis of line assignments. However, the intensity distribution is expected to be substantially different for these two possibilities at low values of K_a . By simulating the band contour using a computer programme to generate all lines of significant intensity, it may be clearly seen that the band is of type-C (Fig. 1c). Thus this spectrum also arises from a ${}^1A''-{}^1A'$ transition. Once the band type had been determined it was then possible to obtain accurate rotational constants from

all the unblended lines (Table I), 1396 assigned lines being fitted to $\pm 0.015\text{ cm}^{-1}$.

TABLE I

A comparison between rotational constants of HNO and of NSF (000 levels, cm^{-1})

		HNO (^a)	NSF (^b)
$\tilde{A}, {}^1A''$	A'	22.164	1.055 59
	B'	1.325 5	0.335 26
	C'	1.242 6	0.251 91
$\tilde{X}, {}^1A'$	A''	18.479	1.658 47
	B''	1.411 5	0.290 61
	C''	1.307 1	0.246 61

(^a) Reference [1].

(^b) References [4] and [5].

Many other examples are now known of transitions between two bent states of triatomic molecules which have well developed rotational structure, and which may be analysed using the non-rigid asymmetric rotor model. Thus the $\tilde{A}-\tilde{X}$ transition at 3440 \AA in HNCN shows very little rotational asymmetry or degradation, and has the appearance of a typical infra-red band of a near symmetric top [6]. On the other hand the $\tilde{C}, {}^1B_1-\tilde{X}, {}^1A_1$ transition of H_2O and D_2O at 1250 \AA is strongly asymmetric [7]. Spectra of strongly asymmetric top molecules are now most usually analysed by a stochastic method. A trial spectrum is calculated for assumed rotational constants using a computer to diagonalize the Hamiltonian matrix, and the parameters are refined by an iterative method. The major difficulties in this method arise in choosing sufficiently good initial assumptions such that the iterative process converges, and recognising any rotational perturbation or other deficiencies in the model.

Multiplet states of bent triatomic molecules consisting of light atoms behave according to Hund's case (b). Thus for doublet states the effect of spin-rotation interaction may be taken into account by adding

$$\mathcal{H}_{S-R} = \sum_{\alpha\beta} \varepsilon_{\alpha\beta} N_\alpha S_\beta; \quad (\alpha, \beta = a, b, c) \quad (2)$$

to the rotational Hamiltonian of equation 1. Several such spectra have been successfully analysed, although in the case of HNF [8] and the XH_2 molecules to be discussed below it has been necessary to extend this model to take account of higher order centrifugal stretching effects on the spin coupling and departure from pure case (b). In these molecules many of the rotational levels are approximately represented by the equations for a near prolate top, for which equation 2 leads to :

$$F_1(N, K_a) - F_2(N, K_a) \approx \frac{(N + \frac{1}{2})}{N(N + 1)} \times \left\{ \varepsilon_{aa} K_a^2 + \frac{1}{2} (\varepsilon_{bb} + \varepsilon_{cc}) [N(N + 1) - K_a^2] \right\}. \quad (3)$$

Since in all these cases the dominant spin-rotation constant is ϵ_{aa} , the doublet splitting for the levels with $N = K_a$ is approximately proportional to K_a , but the splitting decreases rapidly with increasing N at constant K_a . This behaviour is illustrated for PH_2 in figure 2. Each sub-state with a given K_a is completely

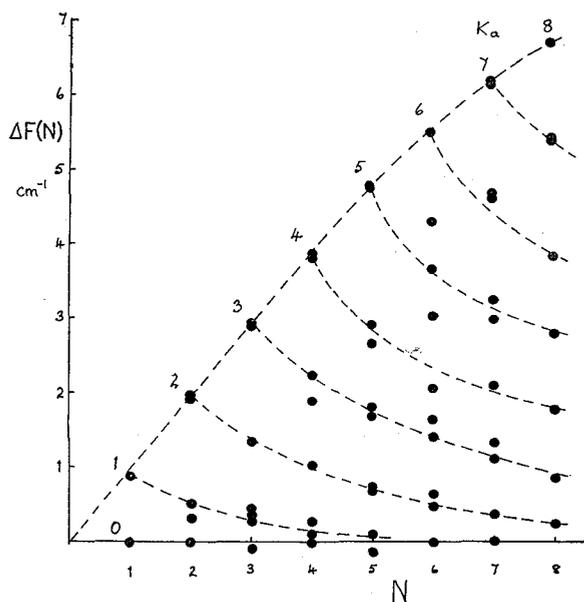


FIG. 2. — Doublet splittings in the 0, 0, 0 level of the $\tilde{A}, {}^2A_1$ state of PH_2 .

analogous to a state of a diatomic molecule which is intermediate between Hund's cases (a) and (b), in which the spin becomes decoupled from the molecular axis with increasing rotation.

Linear Molecules. — The third rotational degree of freedom of a bent triatomic molecule is replaced by angular degeneracy of the bending vibration in a linear molecule. The angular momentum of this vibration may couple with orbital angular momentum (Renner-Teller effect) due to the resolution of the orbital degeneracy when the molecule bends. There are three possible types of potential surface for the variation of the energy of a degenerate state with the amplitude of bending: (a) both component states have linear equilibrium configurations; (b) the upper component is linear, but the lower energy component has a bent equilibrium configuration; and (c) both components are bent.

The effect of the coupling for a ${}^1\Pi$ state of case (a) was evaluated theoretically by Renner [9] in terms of a coupling parameter ϵ , where the two component potentials as a function of the bending coordinate q_2 are:

$$V^\pm(q_2) = \frac{1}{2}f_{22}q_2^2(1 \pm \epsilon). \quad (4)$$

The electronic angular momentum $l\hbar$ may either add or subtract from the vibrational angular momentum $l\hbar$ to give a resultant $K\hbar$ with $K = |l \pm l|$. An important

feature of this theoretical analysis is that the Σ^+ and Σ^- vibronic levels are each dependent on only one component potential function V^+ or V^- , being given by

$$G^\pm(v_2) = \omega_2(v_2 + 1)(1 \pm \epsilon)^{\frac{1}{2}} \quad (5)$$

whereas all levels with $K \geq 1$ are dependent on both potential functions. An excellent example of the Renner effect is given by the $\tilde{A}, {}^1\Pi_u - \tilde{X}, {}^1\Sigma_g^+$ transition of C_3 at 4 050 Å [10]. On account of the very low value of $\nu_2''(63 \text{ cm}^{-1})$ this spectrum contains very many hot bands and transitions with $\Delta v_2 > 0$. Figure 3 shows

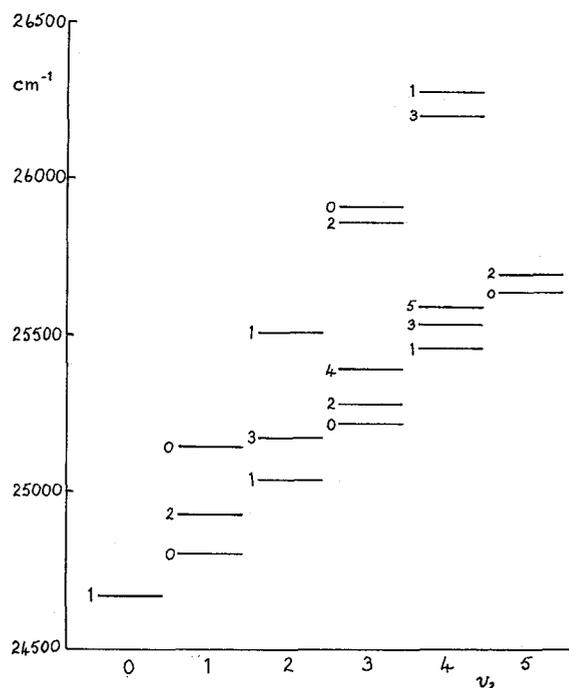


FIG. 3. — Observed vibronic levels for the $\tilde{A}, {}^1\Pi_u$ state of C_3 , ($0, v_2 0$ levels). Each level is labelled by the value of K .

the manifold of observed vibronic levels for the upper state bending vibration. The individual bands in the spectrum have the usual P, Q, R structure of perpendicular transition. However, the rotational structure is considerably complicated by a large l -type doubling and l -uncoupling in the ground state, which are a consequence of the low value of ν_2'' .

The Renner-Teller model. — The basic model which Renner and Teller introduced for vibronic coupling in linear molecules assumes that the two components of an orbitally degenerate state remain in the relationship of « pure precession » with respect to the linear axis even when the molecule is bent: Thus if α is the angle conjugate to the electronic angular momentum in a coordinate system rotating with the nuclei:

$$\begin{aligned} \psi_e^+ &= \psi_e \cos \alpha \\ \psi_e^- &= \psi_e \sin \alpha. \end{aligned} \quad (6)$$

The vibronic Hamiltonian for the bending vibration may then be approximated as :

$$\begin{aligned}\mathcal{H} &= \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2[\exp(2iA\alpha) + \exp(-2iA\alpha)] \\ \mathcal{H}_0 &= V_0(q_2) + \frac{p_2^2}{2\mu_{22}} + \frac{p_\varphi^2}{2\mu_{22}q_2^2} \\ \mathcal{H}_1 &= \frac{1}{2}[V^+(q_2) + V^-(q_2)] - V_0(q_2) \\ \mathcal{H}_2 &= \frac{1}{2}[V^+(q_2) - V^-(q_2)].\end{aligned}\quad (7)$$

With $V_0(q_2) = \frac{1}{2}f_{22}q_2^2$ \mathcal{H}_0 becomes the two dimensional harmonic oscillator Hamiltonian. Renner assumed harmonic potential functions and chose V_0 such that \mathcal{H}_1 vanishes and by a perturbation expansion obtained for the levels with $K = v_2 + 1$;

$$G(v_2, K) = \omega_2 \left[(v_2 + 1) - \frac{1}{8}\varepsilon^2 K(K + 1) \right] \quad (8)$$

and for the remaining pairs of levels with $K > 0$;

$$\begin{aligned}G^\pm(v_2, K) &= \omega_2(v_2 + 1) \left(1 - \frac{1}{8}\varepsilon^2 \right) \pm \\ &\pm \frac{1}{2}\omega_2\varepsilon[(v_2 + 1)^2 - K^2]^{1/2}.\end{aligned}\quad (9)$$

Herzberg et. al. [10] used equations 5, 8 and 9 in their analysis of the vibronic structure of the \tilde{A} , ${}^1\Pi_u$ state of C_3 . The Σ^+ and Σ^- levels lead to

$$\omega'_2 = 307.9 \text{ cm}^{-1}, \quad \varepsilon' = +0.537. \quad (10)$$

These equations give a good representation of the Σ levels, but the deviations between observed and calculated term values increase with increasing K and v_2 , as expected from the neglect of terms higher than harmonic in the basic model and the restricted perturbation expansion.

This basic model has been extended by Pople [11] and Hougen and Jesson [12] to include spin orbit coupling and vibrational anharmonicity, and by Hougen [13] and Johns [14] to take account of rotation and the associated K doubling in Π levels and spin uncoupling in Σ levels. The resultant term value expressions lead to very satisfactory representations of the observations for many linear triatomic molecules, such as NCO [15], BO_2 [16], N_2O^+ [17], and NCN [18]. Nevertheless, there is evidence that this model is over simplified. The \tilde{A} , ${}^2\Sigma^+ - \tilde{X}$, ${}^2\Pi$ band system of NCO includes several bands with $\Delta v_2 = \pm 1$. These transitions would be strictly forbidden if the vibronic interaction arose purely from the \mathcal{H}_2 term in the Hamiltonian of equation (7), but can occur if either the Σ or the Π state mix with other states as the molecule bends. Such mixing appears to be particularly important in NCS, for which the origins of the A , ${}^2\Pi$ and B , ${}^2\Sigma^+$ states only differ by 790 cm^{-1} [19].

Quasi-linear behaviour. — In certain electronic states a number of triatomic molecules do not have energy levels which conform to either of the limiting linear or strongly bent models, but are intermediate between these. This is particularly true of hydrides and dihydrides for which large amplitudes may be excited in the bending vibration even at low values of v_2 . There are two striking consequences of this large amplitude for a state with a bent equilibrium configuration : (a) with increasing v_2 the centrifugal distortion associated with the axial rotational angular momentum $K_a \hbar$ increases dramatically, and (b) the vibrational interval $\Delta G(v_2)$ decreases with increasing v_2 at low values of v_2 , but then increases as the vibrational energy exceeds the barrier to linearity [20]. For the energy levels above this barrier the dependence of the energy on K_a approaches $\omega_2 K_a$ as for a linear molecule, rather than AK_a^2 as for a bent molecule.

Thus, for the \tilde{A} , ${}^2A_1 - \tilde{X}$, 2B_1 system of PH_2 the 0-0 band was analysed using the non-rigid doublet state Hamiltonian of equations (1) and (2) with the addition of the higher power terms $H_K N_a^6 + \eta_{aaa} N_a^3 S_a$ [21]. However, the appearance of the bands changes rapidly with increasing v'_2 , and even for $v'_2 = 3$, which has an energy only half-way up the barrier hindering linearity, this model can no longer represent the observed term values with any accuracy [22]. Furthermore, whereas the spin splitting in PH_2 is sufficiently small that Hund's case (b) is appropriate, for the heavier molecule AsH_2 the spin doubling is closer to Hund's case (a) for each K_a value, with strong uncoupling at higher N corresponding to

$$Y_a = \frac{\varepsilon_{aa} K_a}{B}$$

varying between 1 and 10 for various v_2 and K_a [23].

A semi-quantitative calculation by Dixon [20] of the energy level scheme for a quasi-linear molecule was based on the use of rectilinear bending vibrational coordinate and a model potential function of the form :

$$V(q_2) = \frac{1}{2}kq_2^2 + \alpha \exp(-\beta q_2^2). \quad (11)$$

The eigenvalues for this model were calculated numerically using a computer, and reproduced the features discussed above in a qualitative manner. Thus from the minimum in the curve of $\Delta G'(v_2)$ plotted against $G'(v_2)$ for both PH_2 and PD_2 it was seen that the barrier hindering linearity in the \tilde{A} state is about 6000 cm^{-1} . For PH_2 the levels with $v'_2 = 6$ and 7 are close to the top of this barrier, and the Franck-Condon distribution in the $\tilde{A} - \tilde{X}$ transition is such that bands are observed with v'_2 up to 10.

More rigorous Hamiltonians using a curvi-linear bending coordinate have been developed by Thorson and Nakagawa [24], Freed and Lombardi [25] and Hougen et al. [26]. The latter authors have made a quantitative test of their Hamiltonian for the levels

of the $\tilde{A}, ^1A''$ state of HCN and DCN, and have demonstrated the necessity of using curvilinear coordinates for large amplitudes of bending.

The essential difference between the methods of analysis of the energy levels for linear, for bent, and for-quasilinear molecules are as follows. For linear molecules the rotational structure associated with each set of vibrational quantum numbers v_1, v_2, v_3 and K are analysed in terms of one rotational quantum number J (or N and J in a multiplet state) using a separate set of rotational constants for each level, and the vibrational level origins are then analysed in terms of v_1, v_2, v_3 and K using equations derived from a perturbation expansion. For bent molecules the procedure is the same except that K is now a rotational quantum number; the vibrational levels are defined by v_1, v_2 and v_3 , and the rotational structure is analysed in terms of quantum numbers J, K_a and K_c using the asymmetric top Hamiltonian (and also N for a multiplet state). However, for a quasi-linear molecule there is no acceptable perturbation expansion for the K - and v_2 -dependence of the total energy. It is therefore necessary to analyse the rotational structure as for a linear molecule, but use numerical methods to derive a potential function appropriate to the vibrational origins associated with the quantum numbers v_1, v_2, v_3 and K . For the molecules which have been considered to date it has proved possible to make use of a « high frequency approximation » to separate the stretching and bending motions, the numerical analysis being employed only for the K - and v_2 - contributions to the total energy.

For the $\tilde{A}, ^2A_1$ state of PH_2 it is necessary to extend the model of references [24], [25] or [26] by the addition of the spin doublet splitting and the consequences of the Renner-Teller vibronic interaction associated with the convergence of the $\tilde{A}, ^2A_1$ and $\tilde{X}, ^2B_1$ state of bent PH_2 to a common $^2\Pi_u$ state of linear PH_2 . Since the dominant spin coupling is to the a -axis the doublet splitting can be represented by a modified Hill and Van Vleck formula [27]

$$F_1(N, K) = \bar{B}[(N+1)^2 - K^2] - [\bar{B}^2(N+1)^2 + E(E - 4\bar{B}K)]^{1/2}$$

$$F_2(N, K) = \bar{B}[N^2 - K^2] + [\bar{B}^2 N^2 + E(E - 4\bar{B}K)]^{1/2} \quad (12)$$

where for low values of v_2 :

$$E \sim \varepsilon_{aa} K_a + \eta_{aaaa} K_a^3 \dots \quad (13)$$

In this manner J.-M. Berthou has been able to make a systematic analysis of the rotational structure of the levels of the \tilde{A} state with $v_2' = 1$ to 5, despite many small perturbations [22]. Comparison of figures 2 and 4 indicate how markedly the doublet splitting changes with increasing v_2' .

I have attempted to develop a vibronic model which will collate and combine the sub-level origins and

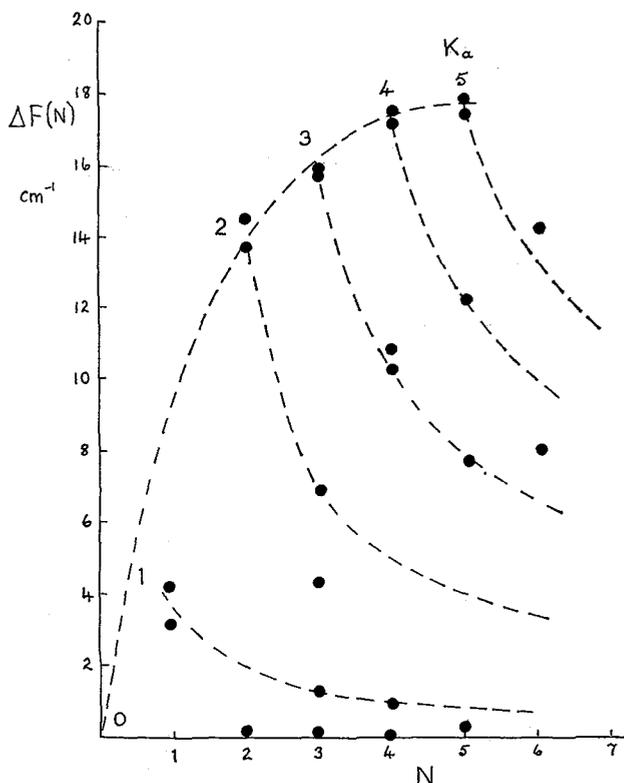


FIG. 4. — Doublet splittings in the 0, 5, 0 level of the $\tilde{A}, ^2A_1$ state of PH_2 .

doublet splitting parameters derived from this analysis. The basic differential equation for the bending and a -axis rotation of an XY_2 molecule derived from the Hamiltonian of Freed and Lombardi [25] by adding second order contributions from the stretching motions, which were assumed to be harmonic and of high frequency compared with the bending vibration (the resulting equations are then almost equivalent to those of Hougen, Bunker and Johns [26]). Thus, with $r = r_0(XY)$, $\theta = (\pi - YXY)$, and φ as the azimuthal angle about the a -axis :

$$\frac{\mathcal{H}_{\text{bend}}^{(0)}}{hc} = g^0(\theta) \left[\frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} \right] - \left[\frac{\partial^2}{\partial \theta^2} + \frac{\cos \theta}{\sin \theta} \frac{\partial}{\partial \theta} \right] g^0(\theta) - A(\theta) \frac{\partial^2}{\partial \varphi^2} + V(\theta)$$

$$g^0(\theta) = \frac{\hbar^2}{2 hcr^2} \frac{[m_x + m_y(1 + \cos \theta)]}{m_x m_y}$$

$$A(\theta) = \frac{\hbar^2}{2 hcr^2} \frac{(m_x + 2m_y)}{m_x m_y(1 - \cos \theta)} \quad (14)$$

Taken to second order in bend-stretch interaction assuming harmonic stretching vibrations at each θ

$$g^0(\theta) \rightarrow g^{(2)}(\theta) = \frac{\hbar^2}{2 hcr^2} \frac{(m_x + 2m_y)}{m_y [m_x + m_y(1 - \cos \theta)]}$$

$$V(\theta) \rightarrow V_{\text{eff}}^{(v_1, v_3)}(\theta) \quad (15)$$

(In these equations $g(\theta)$ and $A(\theta)$, which are angular dependent, are the G -factor for the bending vibration and a -axis rotational « constant » respectively). The vibronic interaction and doublet splitting were added assuming correlation of the \tilde{A} and \tilde{X} states with a common ${}^2\Pi_u$ state and retaining the approximation of « pure precession ». This results in coupled equations for the vibronic levels of the upper and lower states. However these may be approximately uncoupled by diagonalising the effective potential energy matrix

including the a -axis rotation at each θ , and retaining only the resultant equation appropriate to the upper state. Trial calculations based on the eigenvectors of the 2×2 potential energy matrix showed that the maximum errors associated with dropping the remaining off-diagonal nuclear kinetic energy operators were about 30 cm^{-1} , leading to a slight error in the derived potential energy function. Thus with $T(\theta)$ as the kinetic operator from equation (15), and in a basis of bent-molecule electronic wave-functions, the vibronic wavefunctions are solutions of :

$$\begin{bmatrix} T(\theta) + V^+(\theta) + A(K^2 + \Lambda^2) - E, & 2 iAKA \pm \frac{1}{2} i\zeta\Lambda \\ - 2 iAKA \mp \frac{1}{2} i\zeta\Lambda, & T(\theta) + V^-(\theta) + A(K^2 + \Lambda^2) - E \end{bmatrix} \begin{bmatrix} \chi^+(\theta) \\ \chi^-(\theta) \end{bmatrix} = 0 \quad (16)$$

where

$$\langle {}^2B_1 | L_a | {}^2A_1 \rangle = i\hbar\Lambda \quad (17)$$

and A , Λ and ζ are all functions of θ .

Levels of the upper state are therefore approximately given as eigenfunctions of

$$\mathcal{H}_{\text{eff}}^+ \approx T(\theta) + \frac{V^+(\theta) + V^-(\theta)}{2} + A(K^2 + \Lambda^2) + \left[\left\{ \frac{V^+(\theta) - V^-(\theta)}{2} \right\}^2 + \left\{ 2AK \pm \frac{1}{2}\zeta \right\}^2 A^2 \right]^{1/2}. \quad (18)$$

TABLE II

Observed and calculated vibronic term values for the $0, v_2, 0$ levels of the \tilde{A} , 2A_1 state of PH_2 (cm^{-1}). Each set of three entries corresponds to T (obs.), T (calc.)^(a), ΔT (obs.-calc.)

$v_2 \backslash K$	0	1	2	3	4	5
0	18 276.6	18 296.8	18 357.6	18 457.4	18 594.7	18 767.7
	18 276.5	18 297.0	18 358.0	18 458.3	18 596.5	18 770.3
	(0.1)	(- 0.2)	(- 0.4)	(- 0.9)	(- 1.8)	(- 2.6)
1	19 225.9	19 248.8	19 318.3	—	—	—
	19 225.1	19 248.3	19 317.2	19 429.6	19 582.7	19 773.6
	(0.8)	(0.5)	(1.1)	—	—	—
2	20 165.5	20 193.6	20 274.9	20 406.0	20 580.4	20 794.2
	20 165.5	20 192.7	20 272.5	20 400.9	20 573.1	20 784.6
	(0.0)	(0.9)	(2.4)	(5.1)	(7.3)	(9.6)
3	21 094.1	21 129.0	21 227.8	21 382.5	21 581.3	21 819.7
	21 095.4	21 128.8	21 224.8	21 374.8	21 571.0	21 807.0
	(- 1.3)	(0.2)	(3.0)	(7.7)	(10.3)	(12.7)
4	22 009.7	22 055.5	22 180.5	22 363.2	22 591.0	22 856.2
	22 011.5	22 056.5	22 176.9	22 355.6	22 580.9	22 845.2
	(- 1.8)	(- 1.0)	(3.6)	(7.6)	(10.1)	(11.0)
5	22 911.6	22 974.8	23 134.9	23 353.4	23 613.0	23 905.5
	22 910.6	22 978.0	23 134.7	23 349.6	23 608.8	23 904.1
	(+ 1.0)	(- 3.2)	(0.2)	(3.8)	(4.2)	(1.4)

^(a) Potential parameters (cm^{-1}); $V(\theta_m) = 17 791$, $H = 6 700$, $f_m = 25 450$, $f_c = -45$, $f_{\text{ev}} = 15,000$, $\theta_m = 58^\circ$.

The potential function cannot be uniquely determined from the Σ vibronic levels, just as in a diatomic molecule, where an RKR potential function can only be determined using both vibrational levels and rotational constants. Unfortunately, in this case the levels with $K > 0$ have a large energy contribution from the vibronic interaction (up to 200 cm^{-1}), so that the derived potential functions are necessarily very dependent on the assumed functional form and the accuracy of the treatment of the vibronic interaction. The spin-orbit coupling constant ζ has been taken as 230 cm^{-1} from the \tilde{A} , ${}^3\Pi$ state of PH. The upper state potential function $V^+(\theta)$ has been constructed from a harmonic term plus a Lorentzian barrier, with a small additional cubic term:

$$V^+(\theta) = V^+(\theta_m) + \frac{Hf_m(\theta_m^2 - \theta^2)^2}{[f_m\theta_m^4 + (8H - f_m\theta_m^2)\theta^2]} + f_c\theta^2(\theta_m^2 - \theta^2)^3$$

where H is the barrier height, θ_m is the equilibrium angle and f_m is the harmonic force constant about θ_m . Since the vibronic interaction is only of great importance for small θ , where the upper and lower potential curves converge on one-another, $V^-(\theta)$ was taken to be:

$$V^-(\theta) = V^+(\theta) - f_{ev}\theta^2 \quad (20)$$

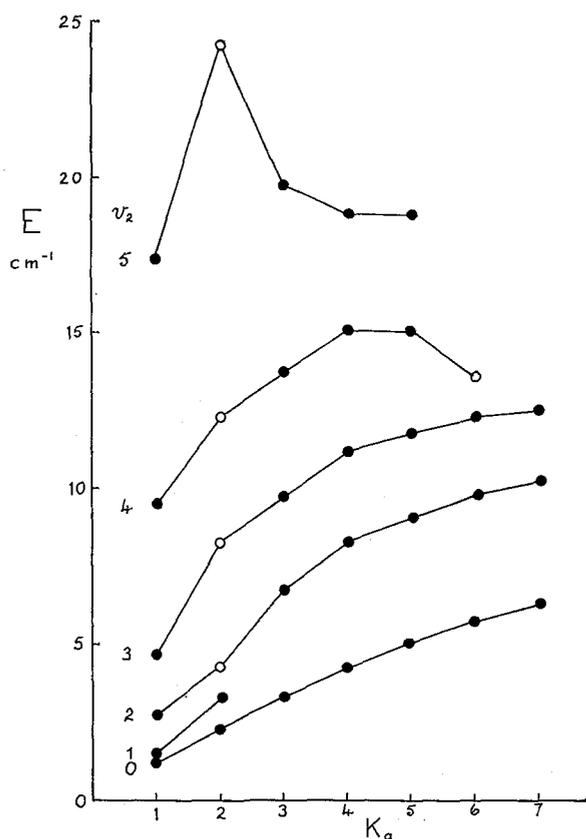


FIG. 5. — Observed spin splitting constants E for the \tilde{A} state of PH_2 derived using equation 12. Points represented by open circles are for sub-states showing substantial perturbations.

and f_{ev} was determined from the separation between the upper and lower curves at θ_m .

Table II gives a comparison between the observed and calculated sub-level origins, the potential function $V^+(\theta)$ having been determined by a least squares fit in which levels with high v_2 and high K were given low weights. The observed and calculated spin doubling constants E are compared in figures 5 and 6.

Clearly the observed trends with increasing v_2 and K are all reproduced, but there are significant deviations between the observations and the calculations, indicating that the model is still not complete. One certain defect is the assumption that the two component states remain in the relationship of « pure precession » when strongly bent. Both published molecular orbitals for a number of XH_2 molecules, and considerations of the magnitudes of the spin coupling constants in the 0, 0, 0 vibronic levels of NH_2 and PH_2 , suggest that the vibronic interaction is only about 60-80 % of that predicted from this model when the valence angle approaches 90° .

The above model is now being applied to other XY_2 molecules such as AsH_2 , SiH_2 and H_2S^+ . The optical spectrum of H_2S^+ is particularly complex, having a

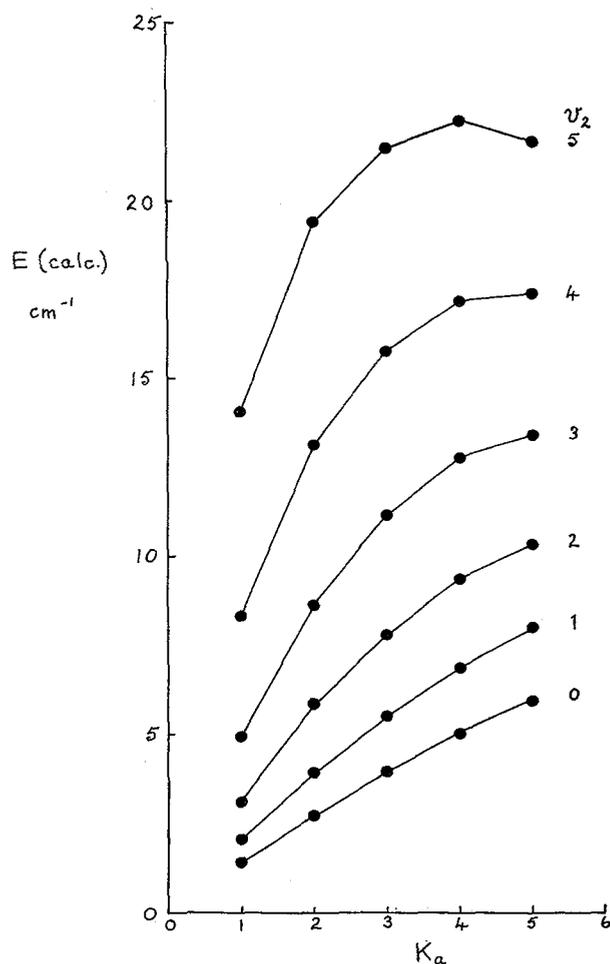


FIG. 6. — Calculated spin splitting constants E for the \tilde{A} state of PH_2 .

similar appearance to the many-line spectrum of H_2 described earlier in this conference, and the assignments can only be made by comparison with the results of model calculations.

Summary. — It can be fairly stated that we understand the behaviour of triatomic molecules undergoing large amplitude motions. That is, the trends and correlations are all explicable, so long as account is taken of vibronic interactions. We also have good quantitative models for the levels of linear and of

strongly bent molecules. However, it has not yet proved possible to derive an accurate quantitative model which will represent all the observed levels of any quasi-linear molecule within the experimental accuracy. This failure to be completely quantitative represents a fundamental difference between diatomic and polyatomic spectroscopy.

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