VIBRONIC COUPLING IN LINEAR MOLECULES AND LINEAR-TO-BENT TRANSITIONS: HCN

H. KÖPPEL
Physik-Department, Technische Universität München, D-8046 Garching, Germany

L.S. CEDERBAUM, W. DOMCKE
Fakultät für Physik, Universität Freiburg, D-78 Freiburg, Germany

and

W. VON NIESSEN
Lehrstuhl für Physikalische Chemie, Technische Universität Braunschweig, D-33 Braunschweig, Germany

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The hamiltonian describing vibronic coupling between Π and Σ electronic states of linear molecules is derived. In contrast to the well-known Renner-Teller coupling of the two components of a Π electronic state, the Σ-Π vibronic coupling term is linear in the bending coordinate. The symmetry properties of the hamiltonian are analyzed. A numerical procedure which allows the calculation of the spectrum (e.g. the absorption or the photoelectron spectrum) for arbitrary values of the coupling constant is presented. The adiabatic potential energy curves are investigated. A nonlinear equilibrium geometry results for the lowest of the interacting states if the vibronic coupling is strong enough. Intensity borrowing effects and non-adiabatic effects due to the vibronic coupling are qualitatively discussed and the importance of the simultaneous coupling to totally symmetric vibrational modes is pointed out. The theory is applied to calculate the vibrational structure of the first band in the photoelectron spectrum of HCN and DCN. The energies and coupling constants entering the hamiltonian are calculated by ab initio methods including the effects of electron correlation. The ab initio calculation predicts strong vibronic interaction between the closely spaced 2Π and 2Σ states responsible for the first band in the photoelectron spectrum. By slightly readjusting some of the parameters excellent agreement between the computed and the experimental spectrum is obtained, confirming that the very complex structure of the spectrum can be fully understood in terms of Σ-Π vibronic coupling and excitation of the CN stretching mode. The second example considered is the 9 eV band in the absorption spectrum of HCN and DCN. The vibronic coupling mechanism explains the experimentally observed strong excitation of the bending mode and the complexity of the vibrational structure of this band.

1. Introduction

Vibronic coupling in linear molecules is generally associated with the Renner-Teller (RT) effect [1]. Renner [2] was the first to examine in detail the interaction between the two components of a degenerate electronic state of a linear triatomic molecule upon executing a bending vibration: due to additional dipole interactions in the bent molecule the degeneracy is lifted and near the linear configuration complicated interactions between the nuclear and electronic motions occur. This leads to a breakdown of the familiar Franck-Condon [3] (FC) and Born-Oppenheimer [4] (BO) approximations.

Subsequently, Renner’s work has been extended to include higher order terms of the interaction [5,6], effects of electron spin [7] and large amplitude of the bending vibration [8]. In ref. [9] the theory has been extended to four-atomic molecules. Rotational energy levels have also been considered [10]. Many experimental observations could thus be satisfactorily explained [1,11].

There have been experimental indications that vibronic interactions of the degenerate state with other electronic states might become important in excitation [12] or ESR [13] spectra. Some selected effects of
such a coupling for $\Pi$ electronic states have been considered by means of perturbation theory, e.g. corrections to rotational energy levels [15,16], contributions to the Zeeman orbital g-factors [14,16] and borrowing effects [16]. A discussion of the weak perturbation of a $\Pi$ electronic state by a $\Sigma$ electronic state has been given recently by Aarts [17].

In the present work the general hamiltonian describing the vibronic interaction of a $\Sigma$ and a $\Pi$ electronic state of a linear molecule is derived. The vibronic interaction of a $\Pi$ state with a $\Delta$ state is discussed elsewhere [18]. We are especially interested in the calculation of electronic spectra (e.g. ionization or excitation spectra) in the case of strong vibronic interaction, where the familiar BO and FC approximations completely break down and perturbation methods are inapplicable. We shall see, in particular, that the excitation of the totally symmetric vibrational modes cannot be treated independently of the vibronic problem. The consideration of the intricate interaction between the vibronically induced vibrational motion and the vibrational motion along the totally symmetric coordinates is prerequisite for the understanding of strong vibronic coupling effects in experimental spectra [22].

Contrary to the Renner-Teller interaction, which is quadratic in the bending coordinate, the $\Sigma$-$\Pi$ (or $\Pi$-$\Delta$, etc.) vibronic interaction is linear in the bending coordinate. We shall see that both the $\Pi$ and the $\Sigma$ electronic state can exhibit a nonlinear equilibrium geometry if the vibronic coupling is sufficiently strong. Thus $\Sigma$-$\Pi$ (or $\Pi$-$\Delta$, etc.) vibronic coupling provides a physical mechanism which explains why many molecules which are linear in their electronic ground state are bent in ionic or excited electronic states. To explain the nonlinearity of $\Pi$-type electronic states the Renner-Teller coupling has been considered [1,5,6].

Contrary to the $\Sigma$-$\Pi$ vibronic coupling mechanism, however, the bending potential energy curves associated with the $\Pi$ electronic state remain harmonic in this case, with possibly a negative force constant for the lower component of the $\Pi$ state. To arrive at a nonlinear equilibrium geometry for the lower component, potential energy terms quartic in the bending coordinate have to be included in an ad hoc fashion [1,5,6].

The nonlinearity of $\Sigma$-type excited electronic states can of course not be explained in this way. The $\Sigma$-$\Pi$ (or $\Pi$-$\Delta$, etc.) vibronic coupling mechanism thus appears conceptually much simpler and more general than the Renner-Teller mechanism for describing linear-to-bent transitions.

The theory will be applied to ionic and excited states of the HCN molecule. Frost et al. [26] have already noted that vibronic coupling between the two closely spaced $^2\Pi$ and $^2\Sigma$ electronic states might be responsible for the considerable complexity of the first band of the photoelectron spectrum of HCN. Here it will be shown that the experimental spectrum can be perfectly reproduced considering the $\Sigma$-$\Pi$ vibronic coupling and its nontrivial modification by the excitation of the totally symmetric CN stretching mode. The second example considered is the 9 eV band in the excitation spectrum of HCN. The observed strong excitation of the bending mode and the complex structure of the band are naturally explained by considering vibronic coupling of the $\Pi$ electronic state responsible for this band with a $\Sigma$ electronic state out of the manifold of $\pi-\pi^*$ excited states as well as excitation of the CN stretching mode.

2. Theory

2.1. The hamiltonian

To derive the hamiltonian which describes vibronic coupling between $\Sigma$ and $\Pi$ electronic states we start from the general expression for the molecular hamiltonian given previously in the second quantization formalism [21]. We neglect the effect of electron spin and confine ourselves to the case where only one $\Sigma$ and one $\Pi$ state are sufficiently close in energy to show consequences of the interaction and where only one degenerate vibration $\nu$ with dimensionless normal coordinates $(Q_1, Q_2)$ couples the two electronic states. In addition, $N$ totally symmetric vibrational coordinates $Q_{1g}, \ldots, Q_{Ng}$ are considered. The harmonic approximation for the electronic ground state potential energy and, temporarily, also the one-particle approximation will be adopted. Considering only that part of the hamiltonian which refers to the interacting states, and retaining only the coupling terms of lowest, i.e. first, order in the normal coordinates we obtain from a straightforward group theoretical analysis in complete analogy to other vibronic coupling cases [22] the following expression
Here the fermion operators \( u_a, v_a \) create (destruct) electrons in one-particle states \( |\psi\rangle \), \( |\psi\rangle \) and \( |\psi\rangle \) respectively. The \( b_s^+ \) and \( b_s^- \) denote phonon creation and destruction operators corresponding to the dimensionless normal coordinates \( Q_s, s = x, y, \ldots \), in the electronic ground state. The quantities \( \omega \) and \( \omega_{i_g} \), \( i = 1, \ldots, N \), are the ground state harmonic frequencies of the bending mode \( \nu \) and the totally symmetric stretching modes \( \nu_{i_g} \). The quantity \( \epsilon_a(0) \) stands for the orbital energy \( \epsilon_a(Q) \), evaluated at the equilibrium geometry of the electronic ground state, \( Q = 0 \). Finally, the linear electron–vibrational coupling constants \( \kappa_i(\sigma) \) are given by [21]

\[
\kappa_i(\sigma) = -2^{1/2} \left[ \partial \epsilon_a(Q)/\partial Q_{i_g} \right] \big|_{Q=0} : \sigma = \pi, \alpha; i = 1, \ldots, N.
\]

An expression for the vibronic coupling constant \( \lambda \) will be given below.

It is easy to interpret the Hamiltonian (1) in physical terms. The first three terms of \( H_1 \) and the first term of \( H_2 \) describe the uncoupled electronic and nuclear motions. The remaining terms describe the interactions between both types of motion. The coupling terms of \( H_2 \) do not mix different electronic states. Elementary symmetry considerations show that only totally symmetric modes can appear in \( H_2 \) [21]. The coupling term in \( H_1 \), on the other hand, describes vibronic interaction of different electronic states via the non-totally symmetric mode \( \nu \). For a given value of \( \lambda \), its importance depends strongly on the energy separation \( \epsilon_a(0) - \epsilon_\pi(0) \). A similar term, linear in \( b_x \) and \( b_y \), also couples \( \Pi \) and \( \Delta \) electronic states [18], but assuming all \( \Delta \) states to be energetically well separated we shall neglect it in this work. Thus, \( H_1 \) is that part of the Hamiltonian specific for the \( \Sigma - \Pi \) vibronic coupling, whereas \( H_2 \) is a general contribution arising from electron–vibrational interaction which is independent of the specific vibronic coupling problem. It is important to note that in the calculation of the spectrum \( H_1 \) and \( H_2 \) cannot be simply separated since they do not commute unless \( \kappa_i(\sigma) = \kappa_i(\pi), i = 1, \ldots, N \).

The discussion has so far been based upon the one-particle approximation. This approximation can be dropped easily as has been demonstrated earlier [21]. Many-body effects are fully included by replacing everywhere in eqs. (1) and (2) the one-particle energies \( \epsilon_a(Q) \) by the negative of the true ionization (excitation) energies, \( -E_{\pi}(Q) \), which can be obtained, for example, as the poles of the one-body (two-body) Green’s function [21]. The analytical structure of the spectrum remains unchanged by the many-body effects.

The Hamiltonian (1) has been written in a real electronic and vibrational basis. However, in this form the symmetry properties of \( H \) are not evident. Since the coupling between the electronic and nuclear motion can depend only on the relative positions of electrons and nuclei, the total energy must be invariant under rotations of the molecule as a whole. Correspondingly, we find by using the usual commutation relations for the boson and fermion field operators that the projection of the total angular momentum on the figure axis \( z \) of the molecule

\[
L_z = \frac{1}{2} \left( b_x^+ b_y - b_y^+ b_x + a_x^+ a_y - a_y^+ a_x \right)
\]

(3)

commutes with \( H \).

Since the vibronic coupling term mixes only states with the same eigenvalue of \( L_z \), the number of non-vanishing non-diagonal matrix elements is minimized by changing to an electronic and vibrational basis where \( L_z \) is diagonal. Defining

\[
b_x^+ = 2^{-1/2} \left( b_x^+ \mp ib_y^+ \right), \quad b_x = 2^{-1/2} (b_x \pm ib_y),
\]

(4a)

\[
a_x^+ = 2^{-1/2} (a_x^+ \pm ia_y^+), \quad a_x = 2^{-1/2} (a_x \mp ia_y),
\]

(4b)

we obtain

\[
L_z = b_x^+ b_x - b_y^+ b_y + a_x^+ a_x - a_y^+ a_y
\]

(5)

Thus, \( b_x^+ \) and \( a_x^+ \),( \( b_x \) and \( a_x \)) are creation (destruction) operators for vibrational quanta and electrons carrying
an angular momentum \( \pm 1 \) along the \( z \) axis. Similarly, \( a_0^+(a_0^-) \) creates (annihilates) an electron with angular momentum zero. In this new complex electronic and vibrational basis the Hamiltonian (1) takes the following form:

\[
H = H_1 + H_2,
\]

\[
H_1 = E_\pi (a_+^* a_+ + a_+^* a_-) + E_0 a_0^* a_0
\]

\[
+ \omega (b_+^* b_+ + b_-^* b_- + 1)
\]

\[
+ \lambda [(a_+ a_0^* + a_0 a_-^*) (b_- + b_+^*)
\]

\[
+ (a_- a_0^* + a_0 a_+^*) (b_+ + b_-^*)],
\]

\[
H_2 = \sum_{i=1}^{N} \omega_i (b_+^* b_+ + \frac{1}{2}) + \sum_{i=1}^{N} \kappa_i(\pi) a_0^* a_0 (b_{ig} + b_{ig}^*)
\]

\[
+ \sum_{i=1}^{N} \kappa_i(\pi) (a_1 a_1^* + a_{-1} a_{-1}^*) (b_{ig} + b_{ig}^*).
\]

Conservation of \( L_z \) is exhibited explicitly by eq. (6b): whenever a coupling term in the square brackets of eq. (6b) raises (lowers) the vibrational angular momentum by one unit through the action of \( b_- \) (or \( b_+ \)), the associated electronic factor lowers (raises) the electronic angular momentum by one unit through the action of \( a_+ a_0^* \) (or \( a_0 a_-^* \)). This shows that the coupling mixes only states with the same eigenvalue of \( L_z \).

### 2.2. The spectrum

We are interested in calculating the spectrum for the transition from an energetically well separated ground state \( |\psi_0\rangle = |0\rangle |\phi_0\rangle \), where \( |0\rangle \) is the vibrational ground state of the neutral molecule and \( |\phi_0\rangle \) is a purely electronic state satisfying \( a_0^* |\phi_0\rangle = 0, \alpha = 0, \pm 1 \). Starting from the golden rule formula, the transition probability as a function of energy \( \omega \) from the initial state \( |\psi_0\rangle \) to the final ionic or excited states can be written as [22]

\[
P(\omega) = \int dt e^{i\omega t} \tau^{+} (0)e^{i\mathcal{H}t} |0\rangle \tau,
\]

\[
|0\rangle = \begin{pmatrix} 1 \ 0 \ 0 \\ 0 \ |0\rangle \ 0 \\ 0 \ 0 \ |0\rangle \end{pmatrix}, \quad \tau = \begin{pmatrix} \tau_0 \ \tau_1 \ \tau_{-1} \end{pmatrix}
\]

With \( \tau_0, \alpha = 0, \pm 1 \) we denote the matrix elements of the electric dipole operator between the initial and the final state. \( \mathcal{H} \) is a matrix Hamiltonian free of electronic operators in analogy to the vibronic coupling problem involving nondegenerate modes [22]. It is given by

\[
\mathcal{H} = \mathcal{H}_1 + \mathcal{H}_2,
\]

\[
\mathcal{H}_1 = \lambda (b_+^* b_+ + b_-^* b_-) \mathbf{1}
\]

\[
= \begin{pmatrix} E_\pi & \lambda (b_- + b_+) & 0 \\ \lambda (b_- + b_+) & E_0 & \lambda (b_- + b_+) \\ 0 & \lambda (b_+ + b_-) & E_\pi \end{pmatrix}
\]

\[
\mathcal{H}_2 = (\Sigma \omega_i b_{ig}^* b_{ig}^*) \mathbf{1}
\]

\[
= \begin{pmatrix} \Sigma \kappa_i(\pi) & 0 & 0 \\ 0 & \Sigma \kappa_i(\pi) & 0 \\ 0 & 0 & \Sigma \kappa_i(\pi) \end{pmatrix}
\]

The Hamiltonian \( \mathcal{H} \), eq. (9), describes the vibrational motion in the ionic or excited states, as well as vibronic coupling between these states. It is to be noted that unless \( \kappa_i(\pi) = \kappa_i(\alpha), i = 1, \ldots, N \), the two parts \( \mathcal{H}_1 \) and \( \mathcal{H}_2 \) do not commute and, therefore, the totally symmetric and bending motions cannot be treated separately.

Let us, for the moment, neglect the coupling to the totally symmetric modes, i.e. \( \kappa_i(\pi) = \kappa_i(\alpha), i = 1, \ldots, N \). Even then, an exact analytical calculation of the spectrum appears to be impossible for any eigenvalue \( l \) of \( L_z \) and perturbation theory breaks down for the values of the parameters of interest. Therefore, one has to resort to numerical methods. To this end we represent \( \mathcal{H}_1 \) as an infinite matrix in an unperturbed two-dimensional harmonic oscillator basis \( |\gamma\rangle = |n_+, n_-\rangle \), where \( n_+ \) and \( n_- \) are the eigenvalues of \( b_+^* b_+ \) and \( b_-^* b_- \), respectively. Each element is still a \( 3 \times 3 \) matrix due to the three electronic degrees of freedom. The re-
resulting supermatrix decouples into an infinite number of pentadiagonal submatrices $M_l$ characterized by the angular momentum quantum number $l$. Only states with angular momenta $l = 0, \pm 1$ can be reached from the unperturbed ground state. Therefore only $M_0$ and $M_1$ are needed. The submatrix $M_0$ can be further reduced by a suitable linear transformation of the degenerate unperturbed states to tridiagonal form [18]. In this latter form it is depicted in fig. 1a. The submatrix $M_1$ cannot be further reduced and is shown in the original basis in fig. 1b. The submatrix $M_{-1}$ is equivalent to $M_1$ in the sense that it can be transformed to $M_1$ by a series of permutations which leave the spectrum unchanged. It is interesting to note that $M_0$ in fig. 1a becomes for $E_a = E_{\pi}$ identical with the secular matrix of the $E \times e$ Jahn–Teller effect for $j = \frac{1}{2}$ [23].

Simple algebra shows that the transition probability (7) is a series of $\delta$-functions at energies equal to the eigenvalues of $M_0$ and $M_1$ with intensities given by the squares of the first components of the corresponding eigenvectors multiplied by $|\tau_0|^2$ and $2|\tau_1|^2$, respectively. The factor 2 arises since $M_1$ is equivalent to $M_{-1}$ and $|\tau_1| = |\tau_{-1}|$. The coupling to totally symmetric modes, which is neglected in the present description, can be simply included by augmenting the unperturbed vibrational basis properly. The resulting secular matrices are not quoted here for the sake of brevity.

The calculation of $P(\omega)$ according to the above scheme is a rather straightforward numerical task if the number of totally symmetric modes involved is not too large; if no totally symmetric modes are included, only tri- and pentadiagonal matrices have to be diagonalized. If the non-symmetry adapted form (1) of the Hamiltonian is used in the numerical calculations, the numerical effort increases by about two orders of magnitude. Even without totally symmetric coupling the calculation of $P(\omega)$ becomes a serious numerical problem. The simplification achieved by the transformation (4) illustrates the importance of the existence of the good quantum number $l$. The situation is formally similar to the $E \times e$ Jahn–Teller problem [23], where the total angular momentum is also a conserved quantity. Of course, the detailed structure of the spectrum is quite different [18], since in the Jahn–Teller case only two electronic states interact, and, moreover, the conserved quantum number is half-integer rather than integer. The $\Sigma - \Pi$ vibronic coupling problem exhibits also some analogies to the vibronic coupling between $B_{1u}$ and $E_{1u}$ states via a degenerate vibration of $E_{2g}$ symmetry, which has been investigated by several authors [43]. Since the $E_{2g}$ mode interacts in first order not only between the $B_{1u}$ and the $E_{1u}$ state, but also within the degenerate $E_{1u}$ state, the B–E problem is more complicated. When the Jahn–Teller splitting of the $E_{1u}$ state is neglected, a conserved quantum number exists which is half-integer as in the Jahn–Teller case [43].

Let us next discuss the adiabatic potential energy surfaces. These are obtained by diagonalizing $K - T_N$, where $T_N$ is the kinetic energy operator for the nuclear motion. If we retain only a single totally symmetric mode $\nu_g$ with harmonic frequency $\omega_g$ and coupling
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Constants $\kappa_\alpha = \kappa_\alpha(\alpha), \alpha = \sigma, \pi$, the potential energy surfaces are given by ($r^2 = Q_\alpha^2 + Q_\beta^2$)

$$V_\pi = -E_\pi + \frac{1}{2} \omega_\pi r^2 + \frac{1}{2} \omega_\sigma Q_\sigma^2 + 2^{1/2} \kappa_\pi Q_\pi^2 \quad \text{(10a)}$$

$$V_\sigma = -\frac{1}{2} (E_\pi + E_\sigma) + \frac{1}{2} \omega_\rho r^2 + \frac{1}{2} \omega_\sigma Q_\sigma^2 + 2^{-1/2} (\kappa_\sigma + \kappa_\pi) Q_\sigma^2$$

$$+ 2^{-1/2} (\kappa_\pi - \kappa_\sigma) Q_\pi^2$$

$$\pm \left(\frac{1}{2} (E_\pi - E_\sigma) + 2^{-1/2} (\kappa_\sigma - \kappa_\pi) Q_\sigma^2 + 2 \lambda^2 \rho^2\right)^{1/2}. \quad \text{(10b)}$$

We note that one of the $\pi$-type potentials, $V_\pi$, is not affected at all by the vibronic coupling. The pair $V_\pi$, however, is for sufficiently large $\lambda$ modified by the vibronic coupling. In particular, the potential energy surfaces $V_\pi$ are anharmonic. The dependence of the last term in eq. (10b) on $Q_\sigma$ leads to a modulation of the bending mode potential with the totally symmetric coordinate. As a consequence the vibrational motions along the bending coordinate and the totally symmetric coordinate are intricately coupled. This non-separability of the modes results from the non-commutativity of the two parts $\mathcal{H}_1$ and $\mathcal{H}_2$ of $\mathcal{H}$, see eq. (9).

For a fixed $Q_\sigma$, say $Q_\sigma = 0$, the lower potential energy $V_\pi$ becomes minimal at a circle around the origin if $4\lambda^2 > \omega_\pi |E_\sigma - E_\pi|$, i.e., a nonlinear equilibrium geometry results from $\Sigma$-$\Pi$ vibronic coupling if $\lambda$ is sufficiently large. Vibronic coupling is thus a fundamental physical mechanism which allows us to understand why many linear molecules are bent in ionic or excited states. According to eq. (10b) it depends only on the relative magnitude of $E_\sigma$ and $E_\pi$ whether the non-linear equilibrium geometry occurs for the $\Sigma$ or the $\Pi$ electronic state. To explain non-linearity in $\Pi$-type electronic states, the Renner–Teller coupling, which is quadratic in the bending coordinate, has been considered [1,5,42]. The adiabatic potentials remain, however, harmonic in this case (with possibly negative force constants) and one has to include anharmonic terms (quartic in $\rho$) in an ad hoc fashion to obtain a non-linear equilibrium geometry [1,5,42]. While the Renner–Teller coupling may be important to explain the non-linearity of isolated $\Pi$ electronic states, $\Sigma$-$\Pi$ vibronic coupling is certainly the dominant mechanism if there are closely spaced $\Sigma$ and $\Pi$ electronic states. In particular, the vibronic coupling mechanism explains also the non-linearity of $\Sigma$-type electronic states. In contrast to previous studies [19,20], where arbitrary functional forms of the potential have been introduced to describe non-linear $\Sigma$-type electronic states, the vibronic coupling mechanism leads to a unique functional form of the bending potential with essentially a single parameter, the vibronic coupling constant $\lambda$ [see eq. (10b)].

Of course, the spectrum is not solely determined by the vibrational levels of the potentials (10) and application of the FC principle. Rather in the numerical solution outlined above borrowing [3] and nonadiabatic [4] effects due to the $Q$-dependence of the electronic wavefunctions are included. These effects are discussed in detail elsewhere [18].

From eq. (10) the ab initio calculation of the vibronic coupling constant $\lambda$ is straightforward. The differences between $V_\pi$, $V_\sigma$ and the ground state harmonic potential are just the ionization potentials or excitation energies $-E_\sigma(Q)$ in the notation of section 2.1. Thus it suffices to calculate these energies at some $Q_\sigma = 0, \rho \neq 0$. $\lambda$ is then obtained from

$$\lambda = \frac{1}{2} \left(\frac{\partial^2}{\partial \rho^2} [E_\sigma(Q) - E_\pi(Q)]\right)^{1/2}. \quad \text{(11)}$$

By $E'_\pi(Q)$ we denote the energy of that component of the $\Pi$ state which transforms totally symmetric under the point group of the bent molecule. The other energy, $E''_\pi(Q)$, must according to eq. (10) remain unchanged; given the transition energies $E_\sigma(Q)$ this provides one with a criterion whether the present theory is applicable for the specific case under consideration.

3. Application to HCN

3.1. The first band in the photoelectron spectrum

The PE spectrum of HCN has been recorded by a number of authors [24–27]. The complexity of the vibrational structure of the first band has lead to the hypothesis that two electronic states, being separated by less than 0.5 eV, occur in that energy range [24]. This view has been confirmed by subsequent ab initio calculations [28,29]. Ionization potentials of $\approx 13.5$ eV and $\approx 13.9$ eV have been obtained for the highest occupied $\pi$ and $\sigma$ orbital, respectively [29]. Irregularities of the vibrational spacings seen in the high-resolution spectrum and the excitation of the bending mode have tentatively been attributed to vibronic interaction...
between the two ionic states \([26,27]\). For illustration and further reference the spectra for HCN and DCN with the highest experimental resolution, obtained by Fridh and Åsbrink \([27]\), are reproduced in fig. 2. The linewidths are different in the HCN and DCN spectra. The spectrum of HCN has been deconvoluted numerically by Fridh and Åsbrink \([27]\) using an instrumental function derived from the xenon peak in the spectrum. This deconvolution procedure has not been performed for the spectrum of DCN.

Since hydrogen cyanide, HCN, is linear in its electronic ground state and the adjacent ionic states are of \(\Sigma\) and \(\Pi\) symmetry, the Hamiltonian (9) with \(N = 2\) applies to the problem. The first step is to calculate the spectrum theoretically, starting from ab initio data for the energies and coupling constants. In the case of the coupling constants for the totally symmetric modes it is advantageous to calculate first the derivatives with respect to suitable internal symmetry coordinates and then transform to normal coordinates via the usual FG-matrix formalism \([30]\). For the construction of the \(L\)-matrix we use the ground state geometry as given by Winnewisser et al. \([31]\) and the force field given by Strey and Mills \([32]\). The harmonic frequencies for the C–H stretching, bending and C–N stretching modes are (values for DCN in parentheses): \(\omega_1 = 0.4267\, (0.3354), \omega_2 = 0.090\, (0.072), \omega_3 = 0.2638\, (0.2424)\) eV, respectively.

The ionization potentials \(-E_a(Q)\) have been calculated on the Hartree–Fock (HF) level (Koopmans’ theorem) and by Green’s function method taking many-body effects into account. The description of both the HF calculation \([29]\) and of the many-body method \([21,33]\) has been given previously and will not be repeated here. In ref. \([29]\) it has been shown that on the HF level the ionization potentials are not accurate and correlation and reorganization effects must be included. Therefore, we quote here only the results of the Green’s function calculation. The calculated energies and coupling constants are (in eV)
\[
-E_a = 13.50, -E_b = 13.92, \kappa_1(\sigma) = 0.004, \kappa_1(\pi) = -0.080, \kappa_2(\pi) = -0.235, \kappa_3(\pi) = 0.057, \lambda = 0.073. \nonumber
\]
Obviously, coupling to the C–H stretching mode \(v_1\) is negligible since \(\kappa_1(\sigma) \ll \omega_1, \alpha \neq \sigma, \pi\). The coupling to the C–N stretching mode \(v_3\), however, cannot be neglected. Since \(\kappa_3(\sigma) \neq \kappa_3(\pi)\) the C–N stretching motion is not separable from the vibronic problem. In the following we omit the C–H stretching mode \(v_1\).

\[\text{Fig. 2. Experimental photoelectron spectrum of HCN (a) and DCN (b) as obtained by Fridh and Åsbrink [27].} \nonumber\]

\[\text{Whereas for DCN the experimentally observed spectrum is shown, the HCN spectrum has been deconvoluted using the line shape of the xenon peak at 13.44 eV as the instrumental function [27].} \nonumber\]

\[\text{The ionization potentials } -E_a(Q) \text{ have been calculated on the Hartree-Fock (HF) level (Koopmans’ theorem) and by Green’s function method taking many-body effects into account. The description of both the HF calculation [29] and of the many-body method [21,33] has been given previously and will not be repeated here. In ref. [29] it has been shown that on the HF level the ionization potentials are not accurate and correlation and reorganization effects must be included. Therefore, we quote here only the results of the Green’s function calculation. The calculated energies and coupling constants are (in eV)} \nonumber\]

\[\begin{align*}
-E_a & = 13.50, -E_b = 13.92, \kappa_1(\sigma) = 0.004, \kappa_1(\pi) = -0.080, \kappa_2(\pi) = -0.235, \kappa_3(\pi) = 0.057, \lambda = 0.073. \nonumber
\end{align*}\]

\[\text{Obviously, coupling to the C–H stretching mode } v_1 \text{ is negligible since } \kappa_1(\sigma) \ll \omega_1, \alpha \neq \sigma, \pi. \text{ The coupling to the C–N stretching mode } v_3, \text{ however, cannot be neglected. Since } \kappa_3(\sigma) \neq \kappa_3(\pi) \text{ the C–N stretching motion is not separable from the vibronic problem. In the following we omit the C–H stretching mode } v_1. \nonumber\]

\[\text{\* To get a consistent analysis of our ab initio data a Hamiltonian } \hat{H}' \text{ describing vibronic and electron-vibrational coupling quadratic in the bending amplitude has to be added to eq. (9). It reads } \nonumber\]

\[\hat{H}' = \begin{pmatrix}
\gamma_1(b_x + b_x^*) & 0 & \delta(b_x - b_z)^2 \\
0 & \gamma_0(b_x + b_x^*) & 0 \\
\delta(b_x + b_x^*)^2 & 0 & \gamma_3(b_x + b_x^*) \\
\end{pmatrix} \times \begin{pmatrix}
(b_x + b_x^*) \\ (b_x + b_x^*) \\
(b_x + b_x^*) \\
\end{pmatrix}. \nonumber\]

\[\text{Whereas the diagonal terms arise in complete analogy to those for totally symmetric modes in the absence of vibronic coupling [21], the nondiagonal terms describe the RT coupling between the two components of the } \Pi \text{ state [11]. Putting } \gamma_0 \text{ for the "nonbonding", } \alpha \text{ orbital equal to zero, the three constants } \gamma_1, \delta \text{ and } \lambda \text{ are obtained from the three ab initio ionization potentials } -E_a(Q) \text{ of the } \Pi \text{ and } \Sigma \text{ type ionic states from a straightforward generalization of eqs. (10) and (11). In this way } \lambda = 0.073 \text{ eV is obtained, whereas } \gamma_1 \text{ and } \delta \text{ are found to be } \approx 0.007 \text{ and } \approx 0.016 \text{ eV, respectively, i.e. roughly one order of magnitude smaller than } \lambda. \text{ Hence, they are neglected in the ensuing calculation, although it cannot be excluded that Renner–Teller coupling influences the multiple-quantum region of the spectrum.} \nonumber\]
from the Hamiltonian and use the notation $\kappa_2, \alpha = \sigma, \pi$ and $\omega_\perp$ for $\kappa_3(\alpha)$ and $\omega_\parallel$, respectively.

Although the calculated vertical ionization potentials are in good agreement with experiment, the vibrational structure calculated using the ab initio data turns out to be in rather poor agreement with the observations. A closer examination reveals that this failure is due to the sensitivity with which the vibrational fine structure depends on the energy difference $E_\sigma - E_\pi$ and the vibronic coupling constant. A similarly critical dependence of the spectrum on these quantities has been found in the case of vibronic coupling problems involving nondegenerate modes [22]. It has been found [22] that both the energy difference and the vibronic coupling constant have to be determined to within $\approx 1\%$ accuracy in order to obtain a spectrum in good agreement with experiment. This hardly seems possible when using a moderate basis set. Therefore, we did not attempt to improve the ab initio calculation, but rather used the present results as a starting point to reproduce the spectrum by readjusting the parameters $E_\sigma, E_\pi$ and $\lambda$. The coupling constants $\kappa_\sigma$ and $\kappa_\pi$ have not been changed. The best result thus obtained for the spectrum is shown in fig. 3a. The values of the parameters used are collected in table 1.

The positions and intensities of the vibrational lines have been calculated as described in section 2.2. The individual lines have been drawn as lorentzians with fwhm $= 0.008$ eV to account for the finite line width in the deconvoluted experimental spectrum fig. 2a. Here and in what follows the absolute magnitudes of the transition dipole matrix elements have been taken to be equal, i.e. $|\tau_1| = |\tau_{-1}| = |\tau_0|$.

To check the significance of our results we have also calculated the coupling constants for DCN from those for HCN given in table 1 by using the isotope rules [30]. In case of the vibronic coupling constant $\lambda$, for example, one obtains from eq. (11) and the requirement that the bending amplitude $b$ be dimensionless

$$\lambda(\text{DCN}) = \left[ (\mu_D + \mu')(\mu_H + \mu') \right]^{1/4} \lambda(\text{HCN}),$$

where $\mu' = \mu_X y^2 + \mu_C (1 + y)^2$, $y = r_{CH}/r_{CN}$ and the quantities $\mu_X, X = H, D, C, N$ and $r_{CX}, X = H, N$ denote the inverse masses and interatomic distances, respectively, in an obvious notation. With regard to the totally symmetric modes the coupling to the CD stretching mode $v_1$ is again found to be small, $|\kappa_1(\alpha)| < 0.1$ eV, $\alpha = \sigma, \pi$, and we neglect it as before. The coupling to the CN stretching mode $v_3$ is nonnegligible as in HCN. The coupling constants $\kappa_\sigma$ and $\kappa_\pi$ for DCN are included in table 1. The resulting spectrum for DCN is shown in fig. 3b. A linewidth of 0.016 eV (fwhm) has been chosen to simulate the limited resolution in the experimental spectrum shown in fig. 2b.

The agreement of the calculated spectra, fig. 3, with the experimental spectra, fig. 2, can be considered as very satisfactory in view of the complexity of the spectra and the simplicity of the Hamiltonian used. The equally good agreement obtained for the spectra

\begin{table}[h]
\centering
\caption{Energies, coupling constants and vibrational frequencies used in the calculation of the photoelectron spectrum of HCN and DCN shown in fig. 3 (in eV)}
\begin{tabular}{cccccccc}
\hline
 & $-E_\pi$ & $-E_\sigma$ & $\kappa_\pi$ & $\kappa_\sigma$ & $\lambda$ & $\omega_\parallel$ & $\omega$
\hline
HCN & 13.8 & 14.0 & 0.235 & -0.057 & 0.090 & 0.264 & 0.090
\hline
DCN & 13.8 & 14.0 & 0.210 & -0.030 & 0.080 & 0.242 & 0.072
\hline
\end{tabular}
\end{table}
of HCN and DCN, which have not been fitted independently, shows that the agreement between theory and experiment is not fortuitous. It is seen that the excitation of the totally symmetric CN stretching mode $\nu_3$ as predicted by the ab initio calculation is only slightly too small. The excitation of the bending mode $\nu_2$ is reproduced almost quantitatively up to about 14 eV and also the irregularities above $\approx 14$ eV can be clearly understood in terms of vibronic coupling effects. Two weak peaks in the low energy part of the experimental spectrum (at 13.55 and 13.76 eV in case of HCN) are not reproduced by the calculation. They presumably represent hot bands [27]. The ab initio value of $\lambda$ differs by about 20% from the fitted value, whereas $E_\sigma - E_\pi$ is wrong by a factor of $\approx 2$. The latter error appears hardly evitable since it arises from subtracting two numbers of roughly equal magnitude, both of which are given to within 2% accuracy.

Having seen that the hamiltonian (9) does account in principle for the complex vibrational structure of the PE spectrum, it is also interesting to see to what extent the details of the structure can be understood in terms of the present vibronic coupling mechanism. The vibrational structure above $\approx 14.0$ eV cannot be reproduced better by simply readjusting the coupling constants since the calculated line spacings differ from the experimental values; an analysis of the low energy portion of the experimental spectrum shows that the CN-stretching frequency $\omega_3$ has decreased upon ionization. This frequency change upon ionization is not accounted for by the hamiltonian (9). It can be included, however, within the present framework in a very simple way [21]: we allow the frequency to vary and keep the ratios $\kappa_\alpha/\omega_\beta$, which determine the excitation strength of the $\nu_\beta$ mode [21], fixed (rather than the coupling constants themselves). When applying this procedure to the CN-stretching frequency $\omega_3$, the bending frequency $\omega$ and the other quantities of table 1 are left unchanged. In this way a value $\omega_3 = 0.225$ eV for HCN and $\omega_3 = 0.210$ eV for DCN has been found to yield the best result. The corresponding spectra are shown in fig. 4.

Comparing the final result, fig. 4, with fig. 2, we see that in the energy region up to $\approx 14.0$ eV the line intensities as well as the line positions agree well with experiment. In the region 14.0--14.2 eV the number and height of the peaks in the spectrum has greatly improved as compared to fig. 3, both for HCN and DCN.

One should note that the shape of the peak at 14.1 eV in the experimental spectrum of HCN could be somewhat erroneous due to uncertainties in the numerical deconvolution procedure [27]. The height of the experimental peaks at 14.27 and 14.24 eV for HCN and DCN, respectively, appears to be an indication that the ab initio coupling constant $\kappa_\sigma$ is somewhat too small. Further smaller discrepancies in that energy range could be due to anharmonicities as well as Renner-Teller coupling neglected here. To summarize these findings, we can be sure to have arrived at a detailed understanding of the origin of the vibronic coupling effects responsible for the complex vibrational structure of first band in the PE spectrum of HCN and DCN.

3.2. The 9 eV band in the excitation spectrum

The valence excitation spectrum of HCN has been a matter of continuous interest over the last 20 years. A detailed study of the long wavelength part of the UV absorption spectrum between 1700--2000 Å was given by Herzberg and Innes [34]. The short wavelength part between 1300--1500 Å was observed very
early by Price and Walsh [35] with photographic techniques: the corresponding transitions were observed more recently in electron energy loss spectra by Tam and Brion [36] and Friddh and Åbrink [27]. From the weakness of the low-energy transitions it has been concluded that they are electronically forbidden at linear geometry, but become allowed because of the nonlinearity of the excited states [34]. The latter conclusion is supported by the strong excitation of the bending mode $\nu_2$ in all valence bands.

Theoretical work has so far concentrated mainly on the attempt to interpret the valence excited states in terms of electron configurations. While Herzberg and Innes [34] had to rely upon Walsh rules [37], later on semi-empirical [38,39] and ab initio CI calculations [40,41] have been performed to obtain the vertical transition energies and the potential energy curves for the bending motion in the excited states. However, there is considerable lack of agreement between the calculations since so many transitions occur in a small energy range [38–41]. Correspondingly, the interpretation of the experiments is still quite ambiguous [27,34,36,38–41].

It is not the purpose of this work to clarify these assignment problems and to perform a detailed ab initio calculation of the excitation spectrum of HCN. Rather, we want to demonstrate that the observed vibrational structure can be understood within the framework of the $\Sigma$–$\Pi$ vibronic coupling mechanism.

We consider the band at $\approx 9$ eV in the excitation spectrum [27]. Two electronic states have been associated with it by Herzberg [42], one of which was supposed to possess a nearly linear equilibrium geometry, the other not. In the ab initio CI-calculation [40] two singlet states were found in the $8$–$9$ eV range, both of which correlate with the $\Pi(\sigma–\pi^*)$ state for linear geometry, in qualitative agreement with the semi-empirical calculations [38,39]. Whereas one component has a linear equilibrium geometry, the other state is bent with an admixture of configurations which correlate with $\pi–\pi^*$ excited configurations at linear geometry. This is precisely the behaviour of the eigenvectors of the $\pi$-type potentials (10) for sufficiently strong coupling if $|E_\alpha| > |E_\gamma|$ and one assumes the $\Pi(\sigma–\pi^*)$ state to be vibronically coupled to the $\Sigma^+(\pi–\pi^*)$ excited state. The latter state was not calculated in ref. [40], but following Åbrink et al. [39] one expects it to lie at $\approx 11$ eV. This assumption is also in accord with a recent CI-calculation of Perić et al. [41], who find that the other $\pi–\pi^*$ excited states occur below $\approx 8$ eV and whose the excited states considered at present above that value. Thus, we attempt to describe the vibrational structure of the valence band by the Hamiltonian (9), putting $-E_\alpha \approx 9$ eV and $-F_\sigma \approx 11$ eV.

To estimate the realistic range of the coupling constant for the totally symmetric modes we note that for transitions from an occupied orbital $i$ to an unoccupied orbital $j$ the linear electron–vibrational coupling constant $\kappa_s(i,j)$ for the mode $\nu_j$ is in zeroth order given by [21]

$$\kappa_s(i,j) = \left[ \frac{\partial (e_j - e_i)}{\partial Q_j} \right]_{Q=0}.$$  \hspace{1cm} (13)

From the concept of bonding and antibonding orbitals one expects, furthermore, that the relation $\partial e^*_\sigma/\partial Q_j \approx -\partial e_\sigma/\partial Q_j$ holds for the orbital energies $e_\sigma (e^*_\sigma)$ of the bonding (antibonding) $\pi(\sigma–\pi^*)$ orbital. This expectation is confirmed by our HF calculation. Since the two orbitals associated with the first band of the PE spectrum of HCN are just the $\sigma$ and $\pi$ orbitals considered here, we can with eq. (13) estimate the coupling constants using the data of section 3.1. Coupling to the $C$–H stretching mode $\nu_2$ should be negligible as in the case of ionization. The coupling constant $\kappa_\pi = \kappa_2(\sigma–\pi^*)$ should be approximately equal to the corresponding coupling constant of the $\Pi$ state of the PE spectrum, the coupling constant $\kappa_\sigma = \kappa_2(\sigma–\pi^*)$ should be roughly twice as large (the index $s$ refers to the $\Sigma^+(\pi–\pi^*)$ excited state, the index $\sigma$ to the $\Pi(\sigma–\pi^*)$ excited state). With these considerations in mind we reduce the number of adjustable parameters by neglecting coupling to $\nu_3$ and putting $\kappa_\sigma = 2\kappa_\pi$ (in fact the vibrational structure was found to be rather insensitive with respect to changes in $\kappa_\sigma$ alone). The remaining four parameters $\kappa_\pi$, $\omega_\pi$, $\omega_\sigma$ and $\lambda$ have been adjusted to obtain good agreement with experiment. The best set of parameters, both for HCN and DCN, is collected in table 2. The value of $\kappa_\pi$ is close to its value for the PE spectrum, as expected. Frequency changes upon excitation are not accounted for by the hamiltonian (9), but are included as described in section 3.1. The resulting spectra for HCN and DCN are displayed, together with their experimental counterparts [27], in fig. 5.

The comparison of the calculated and the experimental spectra shows that good agreement has been obtained: the number, the position and the height of
4. Discussion

In the preceding section we have demonstrated that the vibrational structure of the first band in the PE spectrum and of the 9 eV band in the excitation spectrum of HCN can be well described in terms of $\Sigma$-$\Pi$ vibronic coupling. In the following we investigate in more detail the influence of the vibronic coupling mechanism on the vibrational structure and the adiabatic potential energy surfaces.

The complexity of the photoelectron spectrum of HCN is closely related to the nonseparability of the totally symmetric and the bending modes, i.e., to the noncommutativity of the operators $K_1$ and $K_2$ of eq. (9). To demonstrate this, two additional calculations have been performed, where only one of the two parts of $S$ is included, i.e., either $\lambda$ or $\kappa_\sigma$ and $\kappa_\omega$ are put to zero. The values of the remaining parameters are the same as in table 1. For HCN the two spectra depicted in fig. 6 are obtained. Fig. 6a ($\lambda = 0$) shows the superposition of two Poisson distributions [21], differing

![Diagram](image)

Fig. 6. (a) The photoelectron spectrum resulting when only the coupling to the CN stretching mode is included (i.e., $\lambda = 0$). (b) The photoelectron spectrum resulting when only the vibronic coupling involving the bending mode is included (i.e., $\kappa_\sigma = \kappa_\omega = 0$). The other parameters are the same as in fig. 3a. It is seen that the spectrum resulting from the full vibronic solution (see fig. 3a) is not simply the convolution of (a) and (b). This illustrates the nonseparability of the vibronically active and the totally symmetric modes.
in total weight by a factor of two. Fig. 6b \((k_x = k_y = 0)\) displays the vibrational structure due to the excitation of the bending mode \(v_2\) alone. Clearly, the whole spectrum (fig. 3a) cannot be understood as a convolution of these two individual parts. Rather, in the energy region up to \(\approx 13.95\) eV, one obtains “progressions” in \(v_2\) associated with the \((000)\) and \((001)\) vibrational levels. However, the excitation strength of these progressions is different for the \((000)\) and \((001)\) levels and differs also from that in fig. 6b. In the energy range around \(14\) eV even a complete breakdown of this picture occurs: due to intricate nonadiabatic interactions between the \((0n^2)\) unperturbed levels of the \(\Pi\) electronic state and the \((0m^10)\) levels of the \(\Sigma\) electronic state the levels are mixed and pushed apart, i.e., the intensity is redistributed completely. Thus an interpretation of the vibrational structure in terms of unperturbed vibrational levels as attempted by Fridh and Åsbrink [27] is highly questionable in that energy range. The line at \(13.97\) eV in the spectrum of HCN, for example, gains its intensity by the above mechanism, being a mixture of the \((03^12)\) and \((00^00)\) unperturbed vibrational levels of the \(\Pi\) and \(\Sigma\) electronic states, respectively. This line has previously been attributed [27] to the excitation of \(v_1\), an assignment which is ruled out by the present ab initio calculation of \(\kappa_1(\pi)\).

To gain further understanding of the vibrational structure we have depicted the potential energy surfaces \(V_{\sigma}, V_\pi\) [see eq. (10)] for two different fixed values of the CN stretching coordinate \(Q_g\) as functions of the bending amplitude \(\rho\), using the values of the parameters given in table 1. Fig. 7a shows the bending potentials for \(Q_g = 0\), corresponding to the molecular ground state equilibrium geometry. Fig. 7b shows the potentials for \(Q_g = -1.26\), corresponding to the equilibrium geometry in the ionic ground state. The difference between the bending potentials in fig. 7a and fig. 7b is another manifestation of the nonseparability of the bending and stretching modes. In particular, a nonlinear equilibrium geometry is found for HCN in its ionic ground state when \(Q_g\) is kept fixed at the equilibrium geometry of the neutral ground state. The potential energy of the ionic ground state takes its absolute min-

\[\text{minimum, however, at } Q_g = -1.26 \text{ and } \rho = 0 \text{ (see fig. 7b).} \]

Thus HCN remains linear in its ionic ground state, but the potential energy surface is anharmonic and of a very complicated shape. From the parameters given in table 1 the equilibrium internuclear distances in the ionic ground state are found to be \(r(CH) = 1.090\) Å and \(r(CN) = 1.212\) Å. These values are \(0.025\) Å and \(0.07\) Å, respectively, larger than the internuclear distances in the neutral molecule [31].

The dependence of the potential energy surfaces for the bending motion on the CN stretching coordinate \(Q_g\) leads to another important effect: varying \(Q_g\) towards positive values, the potential curves for \(\rho = 0\) approach more closely and for \(Q_g \approx 0.5\) a crossing of the \(\Pi\)- and \(\Sigma\)-type potentials occurs. The crossing occurs at approximately \(14\) eV and it is clear that near this point non-analyticities of the adiabatic vibrational energies and electronic wavefunctions lead to a breakdown of the familiar BO and FC approximations. Therefore the observed irregularities in the vibrational structure around \(14\) eV are not altogether surprising.

It should be kept in mind that in all the calculations the absolute magnitude of the transition operator matrix elements \(\tau_{\sigma}, eq. (8)\), have been taken to be equal. The band intensities differ by a factor of 2 because of the degeneracy of the \(\Pi\) electronic state. A comparison of fig. 2 and fig. 3 shows that good agreement with experiment is obtained by putting \(\tau_{\sigma} = \tau_{\pi}\). Being not aware of the consequences of the vibrionic coupling one attributes the lines at \(\approx 13.64\) eV and \(\approx 13.85\) eV in the spectrum of HCN, for example, which borrow their intensity from the \(\Sigma\) electronic state, to the \(\Pi\) electronic state. In this way one deduces erroneously a \(\Pi - \Sigma\) intensity ratio of larger than two from experiment [27]. These findings illustrate that great care must be taken in interpreting experimental spectra as complex as the PE spectrum of HCN.

Let us now turn to the valence excitation spectrum. The strong excitation of the bending mode suggests that the lower of the excited states considered is nonlinear at equilibrium. This expectation is confirmed by the calculations: searching the absolute minimum of the lower \(\pi\)-type potential using the values of the parameters given in table 2, we find for the equilibrium coordinates \(a(HCN) = 110.0^0, r(CH) = 1.103\) Å and \(r(CN) = 1.239\) Å. The second component of the \(\Pi\) state remains, according to eq. (10), linear. For this state the equilibrium internuclear distances are found

\[\text{This effect is similar to the modification of the progressions of totally symmetric vibrations in vibronically induced spectra, see ref. [44].}\]
to be $r(\text{CH}) = 1.093 \text{ Å}$ and $r(\text{CN}) = 1.215 \text{ Å}$. Although the vertical excitation energies are the same for both components of the $\Pi$ state, the adiabatic excitation energies differ considerably since the equilibrium geometries are different. For the linear state we obtain an adiabatic excitation energy of 8.87 eV, whereas for the bent state it is considerably smaller, 7.99 eV. These values compare well with the results of Schwenzer et al. [40] for the singlet excited states of HCN: they find a linear state, $3 \, ^1\!A''$, and a bent state, $3 \, ^1\!A'$, with adiabatic excitation energies of 8.97 and 7.85 eV, respectively. The ab initio equilibrium geometries are, however, except for the C–N internuclear distance, in poor agreement with the present results (cf. table 2 of Schwenzer et al. [40]). The discrepancy may be partly due to uncertainties in our numerical values of $E_\sigma$ and $\kappa_\sigma$. Due to the poor resolution of the vibrational structure in the experimental excitation spectra the fitting procedure does not uniquely determine the parameters involved.

It is important to keep in mind that the knowledge of the adiabatic potential energy surfaces is not sufficient to understand the vibrational structure of the spectrum. The $\Sigma$-type electronic state and the two components of the $\Pi$-type electronic state form a vibronic triple rather than three individual states. The neglect of the intricate interaction between the two components of the $\Pi$ state has lead to an erroneous interpretation of the excitation spectrum of HCN [27]: the irregularity of the vibrational structure between $\approx 8.9$ and 9.1 eV has been interpreted as evidence of transitions to the lower vibrational levels of the linear state ($3 \, ^1\!A''$ in the notation of Schwenzer et al. [40]). This kind of reasoning is completely wrong as can be seen by a closer examination of the hamiltonian (9). Although there exist vibrational levels determined by the potential $V_\pi$ [see eq. (10)] alone, they cannot be reached from the ground state of the molecule due to conservation of the total angular momentum $L_z$ [18]. The accessible vibronic levels arise from an interaction between the levels of both $\Pi$ components and cannot be attributed to either of the two $\Pi$-type potential energy surfaces. The numerical calculations show clearly that without the excitation of totally symmetric modes a very regular progression in the bending mode results which shows no indications of perturbations by the vibrational levels of the upper $\Pi$-type electronic state. It is thus clear that the observed irregularities of the spectra (see fig. 5) are merely due to the simultaneous excitation of the bending mode and the totally symmetric stretching mode $v_3$.

Of course the strong nonadiabatic mixing of the two components of the $\Pi$ state is also present in the case of the PE spectrum of HCN, in addition to the nonadiabatic interactions between the $\Sigma$ and the $\Pi$ states mentioned above. This mixing and the conservation of angular momentum account for the fact that despite the existence of two $\Pi$-type potentials in fig. 7 only one progression in $v_2$ is found in the low-energy part ($\omega < 14 \text{ eV}$) of the PE spectrum for a given quantum number of the stretching mode $v_3$.

It is interesting to note that the nonadiabatic mixing of the two $\Pi$-components is independent of the $\Sigma$–$\Pi$ energy separation [18]. While intensity borrowing and nonadiabatic coupling effects become negligible for the $\Sigma$ electronic state if it is sufficiently separated in energy from the $\Pi$ electronic state, the $\Pi$ electronic state can never be described within the adiabatic approximation. The PE spectrum of HCN pro-

![Fig. 7. The adiabatic potential energy curves for the lowest cationic states of HCN as functions of the bending coordinate $\rho = (b_1^2 + b_2^2)^{1/2}$ for (a) $B_0 = 0$ and (b) $B_0 = -1.26$. The three curves represent (from top to bottom) $V_\Sigma$, $V_\Pi^+$, $V_\Pi^-$ [see eq. (10)].](image-url)
vides an example of small $\Sigma-\Pi$ energy separation where neither the $\Sigma$ nor the $\Pi$ state can be described in the adiabatic approximation. In the excitation of HCN, on the other hand, we have found an example of fairly large $\Sigma-\Pi$ energy separation. Here the spectrum belonging to the $\Sigma$ state can be well understood within the adiabatic approximation. As discussed above, however, nonadiabatic coupling effects are still of importance within the $\Pi$ electronic state.

5. Summary

A general hamiltonian describing the vibronic coupling between $\Sigma$ and $\Pi$ electronic states of linear molecules has been derived. Contrary to the well-known Renner–Teller interaction between the two components of a $\Pi$ state, the coupling terms are linear in the bending amplitude. The calculation of the spectrum using this hamiltonian has been discussed in detail. The most important results of the present study are the following:

(i) The projection of the total angular momentum on the molecular axis is a conserved quantity. This leads to a drastic simplification of the eigenvalue problem which thus becomes amenable to a numerical solution for realistic values of the coupling constants.

(ii) The adiabatic potential energy of one of the electronic states involved becomes minimal at a non-linear geometry if the vibronic coupling is strong enough. Both the $\Pi$ and the $\Sigma$ state can become non-linear.

(iii) One of the $\Pi$-type potential energy surfaces is not affected by the vibronic coupling, whereas the other $\Pi$-type potential and the $\Sigma$-type potential become anharmonic. However, the vibronic levels associated with the $\Pi$ electronic state which are accessible from the ground state of the molecule arise from an intimate mixing of both $\Pi$ components and are not attributable to either of the two $\Pi$-type potentials. This nonadiabatic mixing of the two components of the $\Pi$ state is important even when the energy separation between the $\Pi$ and $\Sigma$ electronic states is large and nonadiabatic coupling between the $\Pi$ and $\Sigma$ states is negligible.

(iv) The vibrational motion along the totally symmetric coordinates is in general not separable from the bending motion. This non-separability accounts to a large extent for the complexity of the observed spectra.

The theory has been applied to calculate the vibronic structural of the first band of the photoelectron spectrum of HCN which is associated with two closely spaced electronic states of $\Pi$ and $\Sigma$ symmetry. The energies and coupling constants entering the hamiltonian have been calculated by ab initio methods including the effects of electron correlation. The ab initio calculation predicts the presence of strong $\Sigma-\Pi$ vibronic coupling. It turned out, however, that the ab initio calculation can be hardly made accurate enough to obtain a theoretical spectrum in good agreement with experiment, since the spectrum depends extremely sensitively on the vibronic coupling constant and the energy separation of the interacting electronic states. Starting from the ab initio data, however, we were able to obtain a calculated spectrum in excellent agreement with experiment by an adjustment of some of the parameters. It has been found that the very complex structure of the first band of the PE spectrum can be fully understood in terms of $\Sigma-\Pi$ vibronic effects and the excitation of the totally symmetric CN stretching mode. The equally good agreement with experiment found for HCN and DCN provides an independent test for the correctness of the description since the coupling constants for DCN are related by isotope rules to those for HCN.

As a second example of application the 9 eV band in the excitation spectrum of HCN has been considered. Here no ab initio determination of the parameters entering the hamiltonian has been attempted, but qualitative considerations have been used to reduce the number of free parameters and to limit the range of their values. The typical structure of the band could be well reproduced for both HCN and DCN. The excitation energies and equilibrium geometries derived in this way are partly in agreement with ab initio calculations on the excited states of HCN.

In both examples studied the $\Pi$ electronic state is lower in energy than the $\Sigma$ electronic state. For the excited state of $\Pi$ symmetry one of the two $\Pi$-type adiabatic potential energies becomes minimal at a strongly bent configuration. In the ionic state of $\Pi$ symmetry, on the other hand, HCN remains linear, but with a very complicated and anharmonic shape of the potential energy surface. It may be concluded that $\Sigma-\Pi$ (and $\Pi-\Delta$, etc.) vibronic coupling is the most probable physi-
tical mechanism responsible for the breaking of the line-
earity of molecules upon ionization, excitation or other
electronic transitions.

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