

Interplay between vibronic and spin-orbit couplings in $^3\Pi$ states of triatomic molecules using as an example the $A^3\Pi_u$ electronic state of NCN

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(Received 7 May 2001)

A systematic study of various effects on the structure of the spectra of linear triatomic molecules in the $^3\Pi$ electronic states has been carried out. Particular attention was paid to the interplay between the vibronic and spin-orbit couplings. Variational and perturbative computations at various levels of sophistication were performed for the $A^3\Pi_u$ state of the NCN radical.

Keywords: Renner-Teller effect, spin-orbit coupling, *ab initio* calculations, variational and perturbative approaches.

INTRODUCTION

The non-relativistic and the Born-Oppenheimer (adiabatic)¹ approximation represent the two most important simplifications in the handling of molecular structure and spectra. They are widely used in both the analysis of experimental data and in *ab initio* calculations of spectral features. The general reliability of these approximations is based on the fact that the contribution of non-adiabatic and relativistic effects to the total molecular energy is usually relatively small, at least compared to the energies originating from (non-relativistic) electronic and vibrational degrees of freedom. This particularly concerns species of interest from the point of view of classical (especially organic) chemistry, *i.e.*, "closed-shell" molecules involving "light" atoms (belonging typically to the first two or three rows of the Periodic Table). However, there is a number of important cases where the relativistic and/or adiabatic effects cannot be neglected. In the present study, two of the most common cases are considered. The vibration-electronic (vibronic) interaction within the electronic states spatially degenerate with linear molecular geometry (the Renner-Teller effect²), and the splitting of vibronic levels caused by spin-orbit coupling. These effects determine crucially the structure, energetics, reactivity, and spectra of many free radicals which are of great importance as intermediates in chemical processes and represent key species for understanding of origin of the organic world.

The great majority of the studies on the Renner-Teller effect were carried out for triatomic molecules in doublet Π electronic states. There are several reasons for this. The Renner-Teller effect also occurs in molecules with more than three atoms, but the theory becomes progressively more complicated with increasing number of atoms, and thus of the bending modes which cause the vibronic coupling between the electronic species spatially degenerate with linear geometry. A review of investigations on four-atomic molecules is given in Ref. 3. On the other hand, while many important triatomic radicals have a $^2\Pi$ electronic ground state, corresponding commonly to a single unpaired electron in a π orbital (see, for example, reviews, Refs. 4 and 5), there is a relatively little number of examples for other types of spatially degenerate ground states (Δ , Φ , ...) and other spin multiplicities; the latter involve more than one unpaired electron and/or orbitals other than σ and π ones. In several recent papers the results of variational and perturbative *ab initio* calculations on the $X^5\Delta_g$ ground state of FeH_2 ^{6,7} and the $1^1\Delta_g$ excited state of NCN ⁸ were published. In the present study we concentrate on the interplay between the Renner-Teller effect and the spin-orbit coupling in $^3\Pi$ states of triatomic molecules; we restrict ourselves to the case of relatively weak vibronic interaction, when the splitting of potential surfaces does not lead to a non-linear molecular equilibrium geometry. As a concrete example, the $A^3\Pi_u$ state of the cyanonitrene radical, NCN , is considered.

The low-lying electronic states of NCN have been the subject of extensive *ab initio* computations carried out in our laboratory.^{8,9} In these references, a detailed literature survey is given. Only a few most important papers concerning the $A^3\Pi_u$ state are mentioned. The first observed spectrum of NCN corresponds to the $A^3\Pi_u - X^3\Sigma_g^-$ electronic transition. It was detected in emission by Jennings and Linnet.¹⁰ A detailed analysis of this electronic transition in absorption was carried out by Herzberg and Travis.¹¹ Evidence of the Renner-Teller interaction in the upper state was given. Recent spectroscopic studies in the gas phase performed by McNaughton *et al.*¹² and particularly by Brown *et al.*¹³⁻¹⁶ provided precise values for the rotational constants and bending vibrational frequencies in the $X^3\Sigma_g^-$ and $A^3\Pi_u$ electronic states. An extensive *ab initio* study of several valence-type excited states of NCN was published very recently by Rajendra and Chandra.¹⁷ It involved the determination of the equilibrium geometry, electronic structure and various molecular properties in these species.

The electronic configuration of the low-lying states of NCN is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^2$. This leads to the linear $X^3\Sigma_g^-$, $1^1\Delta_g$ and $1^1\Sigma_g^+$ species. The electronic transitions between the ground state, $X^3\Sigma_g^-$, and the $1^1\Delta_g$ and $1^1\Sigma_g^+$ species are both dipole and spin forbidden. The lowest-lying electronic state into which transition from the ground state is allowed is the $A^3\Pi_u$ state with the leading electronic configuration ... $3\sigma_u 1\pi_u^4 1\pi_g^3$. This transition is the subject of the present study.

Technical details concerning the computation of the bending potential energy curves for the 1^3A_1 and 2^3B_1 states of NCN , correlating at linear geometry with the $A^3\Pi_u$ electronic species, are described in detail in Refs. 8 and 9. The atomic orbital basis consists of 96 Gaussian groups: Both the nitrogen and carbon atoms are described by

the Dunning's (12s 6p 3d) cc-pVQZ AO basis contracted to [5s 4p 3d].¹⁸ The computations are carried out using the MOLCAS program package.¹⁹ The configuration interaction (CI) calculations were performed by means of the DIESEL-MR-CI²⁰ variance of the multi-reference single-and-double excitation configuration interaction (MRD-CI) method of Buenker and Peyerimhoff.²¹ It involves the usual configuration selection and energy extrapolation procedures, accompanied by a perturbative estimation of higher-order electronic excitations with respect to the reference species.²²

HANDLING OF THE RENNER-TELLER EFFECT

Variational approach for handling the Renner-Teller effect in Π electronic states

In the variational treatment of the Renner-Teller effect in the $1^3\Pi_u$ state of NCN, the model Hamiltonian in the form was employed:

$$H = H_e + T_b + T_r^z + H_{SO} \quad (1)$$

H_e is the electronic Hamiltonian including also the nuclear repulsion term. T_b is the kinetic energy operator for the bending vibrations of the nuclei. It involves the derivatives of the coordinate ρ defined as the supplement of the bond angle (in radian) and can be written in the form (in atomic units):

$$T_b = -\frac{1}{2} \left[T_1(\rho) \frac{\partial^2}{\partial \rho^2} + T_2(\rho) \frac{\partial}{\partial \rho} + T_4(\rho) \right] \quad (2)$$

T_r^z represents the operator describing the rotation of the molecule around the (principal) axis z corresponding to the smallest moment of inertia – this axis coincides with a linear nuclear arrangement with the molecular axis. T_r^z can be written in the form:

$$T_r^z = A(\rho) R_z^2 = A(\rho) (N_z - L_z)^2 \quad (3)$$

where R_z represents the z -component of the angular momentum of the nuclei, N_z is the z -component of the total angular momentum excluding spin, and L_z of the electronic angular momentum. A is the rotational constant, $A = 1/2I_{zz}$. The model Hamiltonian (1) commutes with N_z , and thus the quantum number K , corresponding to the latter operator, is a good quantum number. Explicit forms of the coefficients T_i and A depend on the coordinate system employed, the level of approximation applied, *etc.* In the space-fixed coordinate system at infinitesimal bending, the vibrations $T_b + T_r^z$ reduces to the kinetic energy operator of a two-dimensional harmonic oscillator:

$$\lim_{\rho \rightarrow 0} T \equiv T_0 = -\frac{1}{2\mu} \left(\frac{\partial^2}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial}{\partial \rho} + \frac{1}{\rho^2} \frac{\partial^2}{\partial \phi^2} \right) \quad (4)$$

where μ is reduced mass, and ϕ represents the angle between the molecular plane and a space-fixed plane with a common z -axis. H_{SO} represents the leading part of the interplay between the vibronic and spin-orbit couplings assumed in the phenomenological form:

$$H_{SO} = A^{SO} L_z S_z \quad (5)$$

A^{SO} is the "spin-orbit constant", and S_z the z component of the electron spin of the molecule, with the corresponding quantum number S_z' (we use this symbol instead of Σ , because the latter is usually employed to denote $K = 0$ vibronic states); in the case of triplet electronic states, $S_z' = -1, 0$ or 1 . Besides with N_z , the model Hamiltonian (1) also commutes with the projections of the electron spin and the total angular momentum onto the z -axis, J_z ; thus the quantum number P corresponding to J_z ($P = K + S_z'$) is also a good quantum number. The Hamiltonian (1) does not involve the terms describing the stretching vibrations and x, y -rotations. It is supposed that these degrees of freedom can be separated from those contributing directly to the Renner-Teller effect. The wave function corresponding to the Hamiltonian (1) can be written in the form:

$$\Psi_m = \psi_1 f_1^m(\rho, \phi) + \psi_2 f_2^m(\rho, \phi) \quad (6)$$

where ψ_1 and ψ_2 are electronic species, assumed to be eigenfunctions of S_z , and f_1, f_2 are functions of nuclear coordinates [bending (ρ), z rotational (ϕ)]; m is the running index numbering vibronic states corresponding to a particular K value. A convenient electronic basis set for variational treatment of the Renner-Teller effect consists of the functions:

$$\begin{aligned} \psi_1 &= \psi^\Lambda = \frac{1}{\sqrt{2}} e^{i\Lambda\phi} (\psi^+ + \psi^-) \\ \psi_2 &= \psi^{-\Lambda} = \frac{1}{\sqrt{2}} e^{-i\Lambda\phi} (\psi^+ - \psi^-) \end{aligned} \quad (7)$$

where Λ is the quantum number corresponding to L_z . We consider Λ to be an unsigned quantity, in contrast to the quantum numbers K , S_z' , and P , which are assumed to be signed; since the vibronic levels with $|K| \neq 0$ (and $|P| \neq 0$) are always doubly degenerate in the framework of the present model [one state corresponding to $K = +|K|$ and the other to $K = -|K|$ (and analogously for $P = +|P|$ and $P = -|P|$)], we shall deal, as a rule, with non-negative values for K and P only. In the case of Π electronic states, we consider, $\Lambda = 1$. ψ^+ and ψ^- represent the solutions of the electronic Schrödinger equation in the framework of the Born-Oppenheimer approximation (adiabatic electronic functions):

$$H_e \psi^+ = V^+ \psi^+; \quad H_e \psi^- = V^- \psi^- \quad (8)$$

We assume ψ^- to be imaginary. V^+ and V^- are the potentials for the states being invariant and changing sign upon reflection in the molecular plane, respectively. In the one-electron approximation²³ and for $\rho \rightarrow 0$, the electronic functions (7) reduce to:

$$\lim_{\rho \rightarrow 0} \psi^\Lambda = \frac{1}{\sqrt{2\pi}} e^{i\Lambda\theta} \xi(\rho, S_z'); \quad \lim_{\rho \rightarrow 0} \psi^{-\Lambda} = \frac{1}{\sqrt{2\pi}} e^{-i\Lambda\theta} \xi(\rho, S_z') \quad (9)$$

where θ is the azimuthal coordinate conjugated to the electronic angular momentum L_z ($L_z = -i\partial/\partial\theta$), and $\xi(\rho, S_z')$ represents the ρ - and spin-dependent part of the electronic basis functions. Thus in the lowest-order approximation, sufficing for a reliable computation of the contribution of the kinetic energy matrix elements, the

electronic basis functions do not depend on the nuclear angular coordinate ϕ . The vibrational parts, f_1, f_2 , of the molecular wave function are expanded on a basis consisting of the eigenfunctions of the two-dimensional harmonic oscillator with the Hamiltonian $H_0 = T_0 + 1/2k\rho^2$, :

$$\Phi_{\nu,l} = \frac{1}{\sqrt{2}} e^{il\phi} R_{\nu,l}(\rho) \quad (10)$$

where ν (in this section we employ for the bending vibrational quantum number the symbol ν instead of the usual ν_2) is a non-negative integer and l takes the values $\nu, \nu-2, \dots, 1$ or 0 . $R_{\nu,l}$ are defined by:

$$R_{\nu,l} = N_{\nu,l} q^l L_{\nu,l}(q) e^{-\frac{1}{2}q^2} \quad (11)$$

where $L_{\nu,l}$ are the associated Laguerre polynomials in the dimensionless bending coordinate $q \equiv \sqrt{\lambda}\rho$. $\lambda = \sqrt{(k\mu)}$. A convenient choice for k is the force constant corresponding to the mean adiabatic potential $(V^+ + V^-)/2$.

Since the model Hamiltonian (1) commutes with both N_z and J_z , the vibronic/spin-orbit problem can be solved within each K and P (i.e., S_z') subspace separately. Furthermore, the matrix elements of the operators T_b, T_1^z and H_{SO} are diagonal with respect to the quantum number l . The factors $\exp(\pm i\Lambda\phi)$ (Eq. 7) determine the selection rules for the off-diagonal elements of H_e : they do not vanish only between the functions $\Phi_{\nu,l}, \Phi_{\nu,l'}$, with $l' = l \pm 2\Lambda$. This leads to the l values being restricted to $K \pm \Lambda$. In terms of the basis functions chosen, the vibronic wave function (6) has, thus, the form:

$$\begin{aligned} \Psi_{K,S_z',m} = & \psi_1 \frac{1}{\sqrt{2\pi}} e^{i(K-\Lambda)\phi} \sum_{\nu} c_{\nu}^{K,S_z',m,1} R_{\nu,K-\Lambda}(\rho) \\ & + \psi_2 \frac{1}{\sqrt{2\pi}} e^{i(K+\Lambda)\phi} \sum_{\nu} c_{\nu}^{K,S_z',m,2} R_{\nu,K+\Lambda}(\rho) \end{aligned} \quad (12)$$

the expansion coefficient $c_{\nu}^{K,S_z',m,\alpha}$ ($\alpha = 1$ or 2) are obtained by solving in the basis of the bending functions (11) the secular equation with the effective Hamiltonian, obtained after integrating over the spatial and spin electronic coordinates and over ϕ :

$$\begin{aligned} H^{\alpha,\beta} = & \left\{ \frac{V^+ + V^-}{2} - \frac{1}{2} \left[T_1 \frac{\partial^2}{\partial \rho^2} + T_2 \frac{\partial}{\partial \rho} + T_4 \right] - A(K \mp \Lambda)^2 \pm A_{so} \Lambda S_z' \right\} \times \\ & \times \delta_{\alpha,\beta} + \frac{V^+ - V^-}{2} (1 - \delta_{\alpha,\beta}) \end{aligned} \quad (13)$$

To obtain (13), it is assumed that the electronic mean value of the operator L_z is exactly equal to Λ , and neglect the (normally weak) ρ -dependence of A_{SO} . With the help of Eq. (7), the vibronic wave function (12) can be expressed in terms of the adiabatic electronic wave functions:

$$\Psi_{K,S_z',m} = \frac{1}{\sqrt{2\pi}} e^{iK\phi} \left[\Psi^+ f^{K,S_z',m,+} + \Psi^- f^{K,S_z',m,-} \right] \quad (14)$$

where

$$f^{K,S_z',m,\pm}(\rho) = \frac{1}{\sqrt{2}} \left[\sum_{\nu} c_{\nu}^{K,S_z',m,1} R_{\nu,K-\Lambda}(\rho) \pm \sum_{\nu} c_{\nu}^{K,S_z',m,2} R_{\nu,K+\Lambda}(\rho) \right] \quad (15)$$

In the calculations of the present study, two forms of the kinetic energy operator are used. The first one represents the operator for infinitesimal bending vibrations (T_0 given by Eq. (4)). The second one is the rigid bender operator derived by Hougen *et al.*,²⁴ allowing for a treatment of the large-amplitude bending vibrations at constant bond lengths. The molecular potentials are assumed in the form of polynomial expansions in the coordinate ρ .

Perturbative treatment of the Renner-Teller effect in the $^3\Pi$ electronic states of triatomic molecules

The effective Hamiltonian used in the perturbative treatment of the Renner-Teller effect in Π electronic states of triatomic molecules is of the form $H = H_0 + H'$ with:

$$H_0 = T_0 + \frac{1}{2} \omega q^2, \quad H' = \frac{1}{2} \varepsilon \omega q^2 [e^{2i(\theta-\phi)} + e^{-2i(\theta-\phi)}] \pm A_{SO} S_z' \quad (16)$$

The signs + and – in the last term of the expression for H' correspond to the electronic basis functions ψ_1 and ψ_2 (Eqs. 7), respectively. $\omega = \sqrt{k/\mu}$ is the bending vibrational frequency, and ε the Renner parameter defined as $\varepsilon = (k^+ - k^-)/(k^+ + k^-)$, where k^+ and k^- are (quadratic) force constants for the adiabatic potentials V^+ and V^- , respectively. The zeroth-order vibronic functions $|\pm\Lambda, \nu, l, S_z'\rangle$ are products of the electronic basis functions (7) (ψ_1 corresponds to the quantum number $+\Lambda$, ψ_2 to $-\Lambda$, both of them to the spin quantum number S_z') and the vibrational/z-rotational functions (10). The model Hamiltonian (1) reduces to $H_0 + H'$ in the harmonic approximation, *i.e.*, when the potentials involve only quadratic terms and the zeroth-order kinetic energy operator (4) is used.

The zeroth-order energy of vibronic levels is $E^{(0)} = (\nu + 1) \omega$. It is easy to derive the second order perturbative formulae for the case considered when $\omega \gg \varepsilon \omega, A_{SO}$. For so-called *unique* levels, for which $K = \nu + 1$, the zeroth-order vibronic level (for particular K and S_z' values) is non-degenerate; the zeroth-order vibronic/spin wave function is $|\Lambda, K-1, K-1, S_z'\rangle$ and the second order energy is:

$$E = (\nu + 1) \omega + A_{SO} S_z' - \frac{1}{8} \varepsilon^2 \omega K(K + 1) \quad (17)$$

In all other cases (*i.e.*, for $K < \nu + 1$), the zeroth-order levels are twofold degenerate; the basis functions are $|\Lambda, \nu, K-1, S_z'\rangle \equiv |1\rangle$ and $|\Lambda, \nu, K+1, S_z'\rangle \equiv |2\rangle$. The wave functions corresponding to the first-order energy are:

$$\Psi_1 = c_{11} |1\rangle + c_{12} |2\rangle; \quad \Psi_2 = c_{21} |1\rangle + c_{22} |2\rangle \quad (18)$$

with

$$c_{11} = \sqrt{\frac{a^2 + c^2 + a\sqrt{a^2 + c^2}}{2(a^2 + c^2)}} = c_{22}; \quad c_{12} = -\sqrt{\frac{a^2 + c^2 - a\sqrt{a^2 + c^2}}{2(a^2 + c^2)}} = c_{21} \quad (19)$$

$$a \equiv A_{so}S_z'; \quad c \equiv \frac{1}{2} \varepsilon \omega \sqrt{(\nu + 1)^2 - K^2}$$

The second order perturbative formula for energy reads:

$$E_{1,2} = \omega \left(1 - \frac{1}{8} \varepsilon^2 \right) (\nu + 1) \pm \sqrt{A_{so}^2 S_z'^2 + \frac{1}{4} \varepsilon^2 \omega^2 [(\nu + 1)^2 - K^2]} \mp \frac{\varepsilon^2 A_{so} \omega K (\nu + 1) S_z'}{8 \sqrt{A_{so}^2 S_z'^2 + \frac{1}{4} \varepsilon^2 \omega^2 [(\nu + 1)^2 - K^2]}} \quad (20)$$

Perturbative formulae for the combined effect of the vibronic and spin-orbit coupling were first derived by Pople.²⁵ Curiously enough, the original Pople formula for $K < \nu + 1$ was erroneous (it was corrected in a subsequent paper by Hougen,²⁶ see also Ref. 27), as were the corresponding formulae for the Δ states, derived latter by Merer and Travis²⁸ (see, for example, Refs. 23 and 7).

The perturbative part of the Hamiltonian, H' , involves *two* parts (the first one describing vibronic, the second for spin-orbit coupling) which can be of very different magnitudes, so that the perturbative formulae (17) and (20) are generally only formally second order. They are really such if $\varepsilon\omega$ and A_{so} are of comparable magnitude. For weak spin-orbit coupling compared to the vibronic interaction, *i.e.*, when $A_{so} \ll \varepsilon\omega$, the contribution of both of these effects is better balanced in the expression:

$$E_{1,2} = \omega \left(1 - \frac{1}{8} \varepsilon^2 \right) (\nu + 1) \pm \frac{1}{2} \varepsilon \omega \sqrt{(\nu + 1)^2 - K^2} \mp \frac{\varepsilon A_{so} K (\nu + 1) S_z'}{4 \sqrt{(\nu + 1)^2 - K^2}} \quad (21)$$

than in (20) from which (21) is derived. The coefficients (19) in the first-order vibronic wave functions (18) become then $c_{11} = c_{21} = c_{22}1/\sqrt{2}$, $c_{12} = -1/\sqrt{2}$; each (non-*unique*) vibronic levels is equally shared between the electronic species ψ_1 and ψ_2 , or, in other words, belongs predominantly to one of the adiabatic electronic states. In the opposite case of relatively strong spin-orbit and weak vibronic coupling, $A_{so} \gg \varepsilon\omega$, formula (20) reduces (for $S_z' \neq 0$) to:

$$E_{1,2} = \omega \left(1 - \frac{1}{8} \varepsilon^2 \right) (\nu + 1) \pm A_{so} S_z' \pm \frac{\varepsilon^2 \omega^2 [(\nu + 1)^2 - K^2]}{8 A_{so} S_z'} \mp \frac{1}{8} \varepsilon^2 \omega^2 K (\nu + 1) \quad (22)$$

The coefficients (19) become approximately $c_{11} = c_{22} = 1$, $c_{12} = c_{21} = 0$. This means that the vibronic levels belong now either to the electronic species ψ_1 or to ψ_2 .

In the case when the spin-orbit coupling is much stronger than the vibronic coupling, another partitioning of the Hamiltonian becomes sensible – the spin-orbit operator can be incorporated into the zeroth-order Hamiltonian, *i.e.*,

$$H_0 = T_0 + \frac{1}{2} \omega q^2 \pm A_{\text{so}} S_z; \quad H' = \frac{1}{2} \varepsilon \omega q^2 [e^{2i(\theta - \phi)} + e^{-2i(\theta - \phi)}] \quad (23)$$

This scheme which is often reliable, particularly for molecules involving "heavy" atoms (as for example in the case of FeH_2 , indeed for the $X^5\Delta_g$ state),⁶ has not been considered thus far. The zeroth-order energy levels are now $E^{(0)} = (\nu + 1)\omega \pm A_{\text{so}} S_z'$, and for $S_z' \neq 0$ all vibronic levels are computed in the framework of the perturbation theory for non-degenerate levels. The second order formula for the *unique* levels ($K = \nu + 1$) is:

$$E = (\nu + 1) \omega + A_{\text{so}} S_z' - \frac{1}{8} \varepsilon^2 \omega^2 \frac{K(K+1)}{\omega - A_{\text{so}} S_z'} \quad (24)$$

For other levels ($K < \nu + 1$) one obtains:

$$E_{1,2} = (\nu + 1) \omega \pm A_{\text{so}} S_z' + \frac{1}{8} \varepsilon^2 \omega^2 \left[\pm \frac{(\nu + 1)^2 - K^2}{A_{\text{so}} S_z'} - \frac{(\nu \pm K + 1)(\nu \pm K + 3)}{4(\omega \mp A_{\text{so}} S_z')} + \frac{(\nu \mp K + 1)(\nu \mp K - 1)}{4(\omega \pm A_{\text{so}} S_z')} \right] \quad (25)$$

The formulae (24) and (25) are valid regardless of the relative magnitude of the bending frequency ω and the spin-orbit constant A_{SO} . In the case when $A_{\text{SO}} \ll \omega$ they become identical to the $A_{\text{SO}} \gg \varepsilon \omega$ limit of the formulae (17) and (20).

The case $S_z' = 0$ requires special consideration, because the corresponding formulae cannot be generally obtained from those presented above by substituting $S_z' = 0$ in to them; the correct second order energy expressions are:

$$E = [(\nu + 1) - \frac{1}{8} \varepsilon^2 K(K+1)] \omega \quad (26)$$

for unique levels, and

$$E^{\mp} = \omega \left(1 - \frac{1}{8} \varepsilon^2 \right) (\nu + 1) \pm \frac{1}{2} \varepsilon \omega \sqrt{(\nu + 1)^2 - K^2} \quad (27)$$

for other levels, *i.e.*, there are the same as for singlet electronic states (see, for example Ref. 27).

NUMERICAL RESULTS AND DISCUSSION

The *ab initio* computed bending potential energy curves for the components of the $A^3\Pi_u$ electronic state of NCN show a rather weak splitting, with the totally symmetric component, 1^3A_1 , lying below its 2^3B_1 counterpart. By fitting the *ab initio* com-

puted electronic energies in the range of the bond angle values between 180 and 120° the following quadratic-order polynomials are obtained:

$$\begin{aligned} V^+ &= 0.0471 \rho^2 + 0.0055 \rho^4 \\ V^- &= 0.0669 \rho^2 + 0.0085 \rho^4 \end{aligned} \quad (28)$$

where V^+ and V^- stand, respectively, for the 1^3A_1 and 2^3B_1 species. These expansions correspond to the quadratic force constant $k = 0.114$ for the mean potential, $\bar{V} = (V^- + V^+)/2$, and the Renner parameter $\varepsilon = (k^+ - k^-)/(k^+ + k^-) = -0.1737$. The equilibrium bond lengths in the $A^3\Pi_u$ state of NCN are 2.328 Å, which leads to the reduced mass for infinitesimal bending vibrations in ${}^{14}\text{N}{}^{12}\text{C}{}^{14}\text{N}$ of $\mu = 11.3819$ and the harmonic bending frequency of $\omega_2 = 514.47 \text{ cm}^{-1}$. These results are in reasonable agreement with their experimentally derived counterparts,^{11,27,16} as well as with the *ab initio* calculations by Rajendra and Chandra.¹⁷ Our bending frequency is almost identical to the old experimental results of Herzberg and Travis, $\omega_2 = 510 \text{ cm}^{-1}$,^{11,27} and the *ab initio* calculated value of 515 cm^{-1} .¹⁷ It is somewhat lower than the new experimental result of Beaton and Brown [533.95 cm^{-1}].¹⁶ The agreement is even better for the Renner parameter ($\varepsilon = -0.168$,¹¹ -0.161 ,¹⁷ -0.17066)¹⁶.

In our recent study we carried out computations of the NCN spectrum by employing both the *ab initio* derived potentials (Eq. (28)) and those derived from the experimental findings of Beaton and Brown ($\omega_2 = 533.95 \text{ cm}^{-1}$, $\varepsilon = -0.17066$),¹⁶

$$\begin{aligned} V^+ &= 0.05092 \rho^2 \\ V^- &= 0.07188 \rho^2 \end{aligned} \quad (29)$$

and showed that the results are very similar. Since the main goal of the present study was a systematic analysis of the various factors influencing the features of the spectrum arising by combined vibronic and spin-orbit couplings, we find it plausible to use the quadratic potentials (29) as the starting points, rather than their *ab initio* quartic order counterparts (28).

The current version of the DIESEL-CI program package, employed in the present work, does not involve routines for handling relativistic effects; on the other hand, in the framework of our model only one parameter is needed to describe the major effects of the interplay between the vibronic and spin-orbit effects, namely the value of the spin-orbit coupling constant at the equilibrium (linear) nuclear arrangement. For this reason, in the present study the experimentally derived value $A^{\text{SO}} = -37 \text{ cm}^{-1}$,¹⁶ was used.

The results of variational calculation of the low-lying $K = 0 - 4$ vibronic levels of the $A^3\Pi_u$ electronic state of NCN (with respect to the minimum of the potential surface) are presented in Table I. The potentials given by Eq. (29) are employed. One set of computations was carried out with the kinetic energy operator for infinitesimal bending vibrations (Eq. (4)), in the other one the rigid bender operator of Hougen *et al.*²⁴ was used. The convergence of all results is achieved already with 20 vibrational basis functions for each vibronic symmetry in question. The different forms of the kinetic energy operator do not have any qualitative effect on the structure of the spectrum; the vibronic lev-

els computed employing the large amplitude kinetic energy operator lie below their counterparts generated in computations in which the operator for infinitesimal bending vibrations was used, with discrepancies of roughly 1 %.

The fact that the hierarchy of the energetic effects determines the structure of the spectrum in question, namely the magnitude of the bending frequency (roughly 500 cm^{-1}) vs. $\varepsilon\omega_2$ (about 100 cm^{-1}), as a quantitative measure for the vibronic coupling effects, vs. magnitude of the spin-orbit constant (37 cm^{-1}), is clearly pronounced in the present case (roughly 15:3:1), enables a straightforward assignment of the vibronic states. In Table I, they are assigned according to the value of the corresponding bending quantum number ν_2 (linear notation) and the Born-Oppenheimer electronic state to which they predominantly belong (superscript + for 1^3A_1 , and – for 2^3B_1 species); the *unique* vibronic states, nearly equally shared between both electronic species 1^3A_1 and 2^3B_1 [or, in other words, belonging almost exclusively to the electronic species ψ_1 (Eq. (6))], are denoted by the subscript u . The quantum numbers ν_2 and $+/-$ are generally approximate ones; on the other hand, K and $P = K + S_z'$ are good quantum numbers in the framework of our model. This is also the parity number $+/-$ in the case of $P = K$ (*i.e.*, $S_z' = 0$) spin-vibronic states. The g/u quantum numbers, which lead to trivial additional assignment of vibronic levels (g for even K , u for odd K values), are omitted.

The results presented in Table I represent the typical structure of the spectrum of a linear triatomic molecule in a $^3\Pi$ electronic state. The spin-orbit splitting is most pronounced in *unique* levels, where it is roughly equal to the magnitude of the spin-orbit coupling constant. Since this constant has a – sign, the *unique* levels with the lowest P value for a given K (*i.e.*, those corresponding to $S_z' = -1$) have the highest energy. In the other $K \neq 0$ states (*i.e.*, for $K < \nu_2 - 1$) the spin-orbit splitting is more or less effectively quenched, because of the comparable contribution from both the ψ_1 and ψ_2 electronic basis functions in the corresponding vibronic wave functions. The $K = 0$ levels are split due to the spin-orbit coupling into two levels: corresponding to $S_z = 0$ (*i.e.*, $P = 0$) in non-degenerate, while the other ($S_z = \pm 1$) is doubly degenerate.

The results of perturbative computations according the formulae (17) and (20), in which the same parameters are employed as in the above described variational calculations (in this case only the kinetic energy operator for infinitesimal bending vibrations is used) are presented in Table II. Maximal deviations of these results from their variational counterparts are few wavenumbers, reflecting the fact that the second order perturbation theory is in the present case very reliable, being a consequence of the relative smallness of the perturbing terms.

The qualitative and quantitative features of the vibronic spectrum in $^3\Pi$ electronic states depend on several parameters and we find it instructive to analyze these effects in some details. In the simplest limiting case when the mean bending potential is harmonic, the splitting of the potentials upon bending and the magnitude of the spin-orbit coupling constant are negligible (*i.e.*, $\varepsilon = 0$, $A_{so} = 0$) and the kinetic energy operator is that for infinitesimal bending vibrations (T_0), the vibronic energies depend only on the vibrational quantum number ν_2 , *i.e.*, $E = (\nu_2 + 1)\omega$. Each vibronic level is then $6(\nu_2 + 1)$ -fold degenerate: For

each quantum number ν_2 there is a series of sub-levels with the value of the vibrational angular quantum number $l, l = \nu_2, \nu_2 - 2, \dots, -\nu_2$, the number of them being thus $\nu_2 + 1$. The quantum numbers l combines with the electronic angular quantum number $\Lambda = 1$ into $K = l \pm 1$. In the framework of the present model the energy of vibronic levels never depends on the sign of the quantum number K and in the following we classify the vibronic levels according to the absolute value of K . For each ν_2 value there is one vibronic level with $K = \nu_2 + 1$ (*unique* level) and a pair of levels for each $K = \nu_2 - 1, K = \nu_2 - 3, \dots, K = 1$ or 0 (each $K \neq 0$ level has a $+ |K|$ and a $- |K|$ component). Finally, each K value is combined with the spin quantum number S_z' , with possible values $1, 0$, and -1 , into $P = K + S_z'$. This situation is presented at the left and right edges of Fig. 1.

TABLE I. Vibronic spectrum in the $A^3\Pi_u$ electronic state of NCN, computed variationally employing the following parameters: V^+ (in *hartree*) = $0.05092 \rho^2$, $V^- = 0.07188 \rho^2$, $A_{so} = -37 \text{ cm}^{-1}$. K is the vibronic quantum number; ν_2 the bending quantum number ("linear" notation); S_z' the quantum number for the z component of the electron spin. The superscripts $+$ and $-$ denote vibronic levels belonging (exactly or predominantly) to the 1^3A_1 and 2^3B_1 components of the $A^3\Pi_u$ electronic state, the subscript u stands for *unique* levels. The energy values are in reciprocal centimeters. Zero point on the energy scale corresponds to the minimum of the $A^3\Pi_u$ potential surface. The energy levels given without parentheses were obtained employing the kinetic energy operator for infinitesimal bending vibrations $\mu = 11.3819$, the values in parentheses are the results of computations which employ the rigid bender kinetic energy operator of Hougen *et al.*²⁶

K	ν_2	$S_z' = -1$	$S_z' = 0$	$S_z' = 1$
0	1 ⁺	965.40 (957.81)	972.51 (964.91)	965.40 (957.81)
	1 ⁻	1162.53 (1155.20)	1155.46 (1148.14)	1162.53 (1155.20)
	3 ⁺	1941.51 (1919.86)	1945.02 (1923.35)	1941.51 (1919.86)
	3 ⁻	2314.32 (2293.12)	2310.91 (2289.72)	2314.32 (2293.12)
	5 ⁺	2915.39 (2870.56)	2917.53 (2872.68)	2915.39 (2870.56)
	5 ⁻	3468.31 (3423.95)	3466.37 (3422.05)	3468.31 (3423.95)
1	0 ^u	567.72 (561.10)	530.01 (524.40)	493.27 (487.65)
	2 ⁺	1463.23 (1452.10)	1466.70 (1454.67)	1460.15 (1447.27)
	2 ⁻	1728.30 (1716.12)	1725.20 (1713.93)	1732.00 (1721.58)
	4 ⁺	2434.96 (2404.81)	2436.08 (2405.41)	2431.70 (2400.55)
	4 ⁻	2884.31 (2853.95)	2883.73 (2853.91)	2888.38 (2859.04)
2	1 ^u	1092.21 (1084.76)	1056.09 (1048.65)	1019.86 (1012.42)
	3 ⁺	1969.31 (1954.86)	1969.83 (1953.92)	1962.45 (1945.21)
	3 ⁻	2285.59 (2270.21)	2285.83 (2271.91)	2293.78 (2281.20)
	5 ⁺	2935.30 (2897.11)	2934.04 (2895.00)	2928.32 (2888.47)
	5 ⁻	3446.92 (3408.85)	3449.29 (3412.14)	3455.77 (3419.44)
3	2 ^u	1613.59 (1605.26)	1578.31 (1569.98)	1542.82 (1534.49)
	4 ⁺	2479.79 (2462.31)	2477.42 (2458.13)	2468.64 (2447.72)
	4 ⁻	2838.17 (2821.13)	2841.72 (2826.52)	2851.45 (2837.90)
4	3 ^u	2131.07 (2122.82)	2096.85 (2088.59)	2062.30 (2054.03)
	5 ⁺	2992.70 (2972.50)	2987.46 (2965.25)	2976.99 (2953.00)
	5 ⁻	3387.88 (3370.73)	3394.77 (3379.67)	3406.61 (3393.33)

TABLE II. Vibronic spectrum in the $A^3\Pi_u$ electronic state of NCN, computed in the framework of the second order perturbation theory with the parameters $\omega_2 = 533.95 \text{ cm}^{-1}$, $\varepsilon = -0.17066$, $A_{so} = -37 \text{ cm}^{-1}$. For key to notation see Table I

K	ν_2	$S_z' = -1$	$S_z' = 0$	$S_z' = 1$
0	1 ⁺	965.66	972.89	965.66
	1 ⁻	1162.36	1155.14	1162.36
	3 ⁺	1942.06	1945.78	1942.06
	3 ⁻	2313.99	2310.27	2313.99
	5 ⁺	2916.17	2918.66	2916.17
	5 ⁻	3467.90	3465.41	3467.90
1	0 ^u	567.06	530.06	493.06
	2 ⁺	1463.55	1467.15	1460.33
	2 ⁻	1728.48	1724.89	1731.70
	4 ⁺	2435.37	2436.82	2432.19
	4 ⁻	2884.69	2883.24	2887.87
2	1 ^u	1093.24	1056.24	1019.24
	3 ⁺	1969.46	1970.19	1962.36
	3 ⁻	2286.59	2285.86	2293.68
	5 ⁺	2934.97	2934.30	2928.34
	5 ⁻	3449.10	3449.77	3455.73
3	2 ^u	1615.52	1578.52	1541.52
	4 ⁺	2479.87	2477.78	2468.26
	4 ⁻	2840.19	2842.28	2851.80
4	3 ^u	2133.92	2096.92	2059.92
	5 ⁺	2993.28	2988.28	2976.61
	5 ⁻	3390.79	3395.80	3407.46

Let us consider now the case differing from the above one only in the value of the spin-orbit constant, assumed now to be $A_{so} = -37 \text{ cm}^{-1}$ (instead of zero). The energy levels for this situation are presented in Table III (numbers without parentheses) and by the second column from the left in Fig. 1. Inspection of the structure of secular equation (13) shows that in this case three double degenerate effective bending potentials exist, involving the mean electronic energy and the contribution from the spin-orbit part of the Hamiltonian, with energy spacing equal to $|A_{so}|$: The lowest-energy ones correspond to $\Lambda = 1, S_z' = 1$ and $\Lambda = -1, S_z' = -1$, the next two to $\Lambda = 1, S_z' = 0$ and $\Lambda = -1, S_z' = 0$, and the highest-energy pair to $\Lambda = 1, S_z' = -1$ and $\Lambda = -1, S_z' = 1$. Each zeroth-order vibrational level (corresponding to the case when $A_{so} = 0$) with a particular value ν_2 is now split into three levels, each of which belongs to one of the effective potentials. These levels are generally degenerate, involving all possible K species with the combinations of quantum numbers Λ and S_z' associated with the effective potential in question. The exceptions are the levels corresponding to $\nu_2 = 0$, being non-degenerate (except for the $\pm|K|$ degeneracy). These three Π ($K = 0$) vibronic levels in increasing order of energy correspond to the basis functions $|\Lambda = 1, \nu_2 = 0, l = 0, S_z' = 1\rangle, |1,$

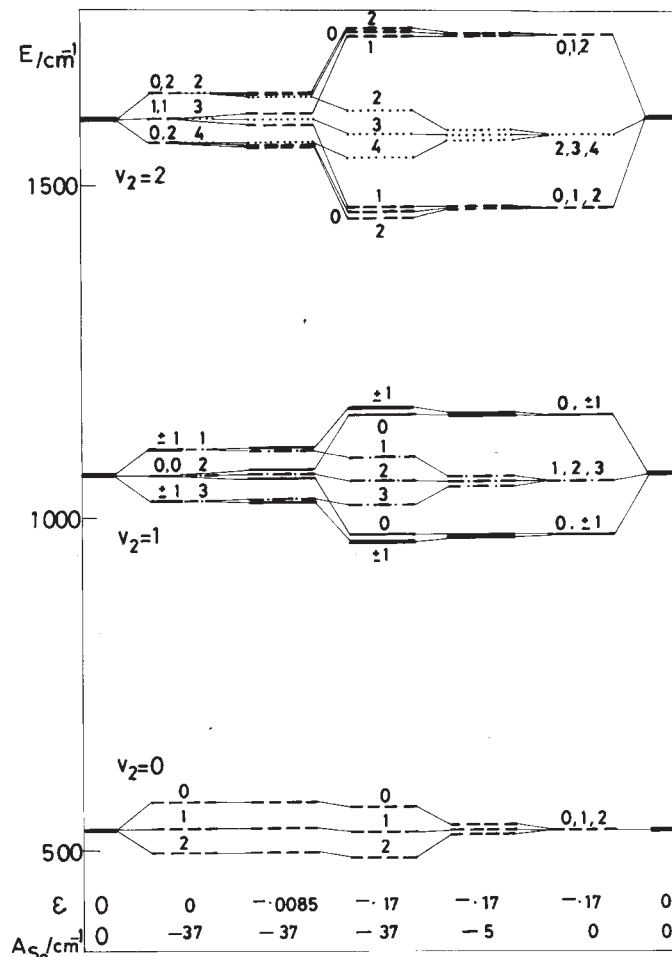


Fig. 1. Low-lying part (for the bending vibrational quantum number $\nu_2 = 0, 1,$ and 2) of the vibronic spectrum of a triatomic molecule in the $^3\Pi$ electronic state with linear equilibrium geometry, computed for various values of the Renner parameter ϵ and the spin-orbit constant, A_{S_0} (in cm^{-1}). The spectrum shown in the center of the Figure ($\epsilon = -0.17, A_{S_0} = -37 \text{ cm}^{-1}$) corresponds to the $A^3\Pi_g$ state of NCN. The zero on the energy scale represents the minimum of the potential energy surface. The solid lines: $K = 0$ (Σ) vibronic levels; the dashed lines: $K = 1$ (Π) levels; the dash-dotted lines: $K = 2$ (Δ) levels; the dotted lines: $K = 3$ (Φ) levels. Levels are denoted by the value of the corresponding quantum number $P (= K + S_z)$.

$0, 0, 0 >$, and $|1, 0, 0, -1 >$. The lowest-energy level corresponding to $\nu_2 = 1$ involves two Σ ($K = 0$) and one Δ ($K = 2$) vibronic states, the wave functions of which are $|1, 1, -1, 1 >$, $|-1, 1, 1, -1 >$, and $|1, 1, 1, 1 >$, respectively. The next level involves $|1, 1, -1, 0 >$, $|-1, 1, 1, 0 >$ Σ , and $|1, 1, 1, 0 >$ Δ species. The highest-energy $\nu_2 = 1$ level comprises $|1, 1, -1, -1 >$, $|-1, 1, 1, 1 >$ Σ , and $|1, 1, 1, -1 >$ Δ vibronic states. Extension of this scheme to higher ν_2 values is a matter of straightforward book-keeping.

TABLE III. Vibronic spectrum in the ${}^3\Pi_u$ electronic state of a triatomic molecule, computed variationally employing the following parameters: V^+ (in *hartree*) = $V^- = 0.0614 \rho^2$, $A_{SO} = -37 \text{ cm}^{-1}$. The energy levels given without parentheses were obtained employing kinetic energy operator for infinitesimal bending vibrations ($\mu = 11.3819$), the values in parentheses are the results of computations which employ the rigid bender kinetic energy operator of Hougen *et al.*²⁶ For key to notation see also Table I.

K	ν_2	$S_z' = -1$	$S_z' = 0$	$S_z' = 1$
0	1	1030.91 (1023.46)	1067.91 (1060.46)	1030.91 (1023.46)
	1	1104.91 (1097.46)	1067.91 (1060.46)	1104.91 (1097.46)
	3	2098.82 (2077.41)	2135.81 (2114.40)	2098.82 (2077.41)
	3	2172.82 (2151.40)	2135.81 (2114.40)	2172.82 (2151.40)
	5	3166.72 (3122.15)	3203.72 (3159.15)	3166.72 (3122.15)
	5	3240.72 (3196.15)	3203.72 (3159.15)	3240.72 (3196.15)
1	0	570.95 (565.34)	533.95 (528.34)	496.95 (491.34)
	2	1564.86 (1556.48)	1601.86 (1586.97)	1564.86 (1549.97)
	2	1638.86 (1623.96)	1601.86 (1593.48)	1638.86 (1630.48)
	4	2632.77 (2605.80)	2669.77 (2636.29)	2632.77 (2599.30)
	4	2706.77 (2673.29)	2669.77 (2642.78)	2706.77 (2679.78)
2	1	1104.91 (1097.46)	1067.91 (1060.46)	1030.91 (1023.46)
	3	2098.82 (2090.41)	2135.81 (2114.40)	2098.82 (2077.41)
	3	2172.82 (2151.40)	2135.81 (2127.40)	2172.82 (2164.40)
	5	3166.72 (3135.09)	3203.72 (3159.15)	3166.72 (3122.15)
	5	3240.72 (3196.15)	3203.72 (3172.09)	3240.72 (3209.09)
3	2	1638.86 (1630.48)	1601.86 (1593.48)	1564.86 (1556.48)
	4	2632.77 (2625.23)	2669.77 (2642.78)	2632.77 (2605.78)
	4	2706.77 (2679.78)	2669.77 (2662.23)	2706.77 (2699.23)
4	3	2172.81 (2164.40)	2135.81 (2127.40)	2098.82 (2090.41)
	5	3166.72 (3160.97)	3203.72 (3172.09)	3166.72 (3135.09)
	5	3240.72 (3209.09)	3203.72 (3197.97)	3240.72 (3234.97)

The introduction of vibronic coupling ($\varepsilon \neq 0$) causes the removal of the above degeneracies and leads to the general vibronic/spin-orbit pattern given in Table I and in the central part of Fig. 1. Each vibronic level is characterized by a particular K and $P = K + S_z'$ quantum number (*i.e.*, by a particular K, S_z' combination). The exception represent the $\Sigma (K=0), P = \pm 1$ levels, remaining degenerate from each other. The composition of the *unique* states remains essentially unchanged with respect to the case of no vibronic coupling. The vibronic wave functions for the other vibronic species are predominantly determined by linear combinations of the basis functions $|\Lambda = 1, \nu_2, l = K - 1, S_z'\rangle$ and $|\Lambda = -1, \nu_2, l = K + 1, S_z'\rangle$. In the case when the vibronic coupling is weak compared to the spin-orbit coupling ($\varepsilon \ll A_{SO}$), the coarse structure of the spectrum is determined by the spin-orbit effects. This is illustrated in Fig. 1 with the case $\varepsilon = -0.0085$ (corresponding

to $\varepsilon\omega = -4.5 \text{ cm}^{-1}$, $A_{SO} = -37 \text{ cm}^{-1}$; note, for example, that the $\nu_2 = 1, K = 0$ levels are divided into three pairs of close-lying levels, with successive energetic separation between these pairs nearly equal to the value of the spin-orbit constant.

Let us now consider the rising of the vibronic/spin-orbit structure from the "opposite side", when the vibronic interaction is dominant with respect to the spin-orbit coupling (right-hand part of Fig. 1). For a non-zero value of the Renner parameter (in the concrete case $\varepsilon = -0.17$) and $A_{SO} = 0$, the vibrational level corresponding to the bending quantum number ν_2 is split into $\nu_2 + 1$ vibronic levels if ν_2 is even, and into $\nu_2 + 1$ levels for odd ν_2 values. Each of these levels is threefold spin-degenerate. The energy of the central level of each ν_2 manifold (*unique* level, $K = \nu_2 + 1$) is relatively little changed with respect to the case of no vibronic coupling. The corresponding vibronic wave function contains almost exclusively the $|\Lambda = 1, \nu_2, l = K - 1, S_z'\rangle$ basis function. Other vibronic levels ($K < \nu_2 + 1$) appear in pairs being roughly symmetrically placed around the unique levels. The corresponding wave functions are predominantly built by linear combinations of the basis functions $|\Lambda = 1, \nu_2, l = K - 1, S_z'\rangle$ and $|\Lambda = -1, \nu_2, l = K + 1, S_z'\rangle$, with the expansion coefficients being of exactly (for $K = 0$) or nearly (for $K \neq 0$) equal magnitude. In contrast to the *unique* levels, which can be looked upon as belonging to the mean bending potential, or in other words, to be equally shared between both A_1 and B_1 components of the Π electronic state, all other vibronic states are associated either exactly (for $K = 0$), or approximately (for $K \neq 0$) with a particular adiabatic electronic state. The Σ ($K = 0$) states can be classified according to their behavior upon reflections in the symmetry planes to Σ^+ (belonging to the A_1 adiabatic electronic state) and Σ^- (belonging to the B_1 state). The non-*unique* vibronic levels corresponding to a particular ν_2 and belonging (predominantly) to a particular adiabatic electronic states lie energetically close to one another, compared with the energy difference between them and the corresponding *unique* level.

When an additional weak spin-orbit coupling is introduced (Fig. 1, $\varepsilon = -0.17$, $A_{SO} = -5 \text{ cm}^{-1}$ case), the spin degeneracy of vibronic levels is removed, but the energy pattern is quite different from that corresponding to the opposite case of strong spin-orbit and weak vibronic coupling discussed above. The coarse structure of the spectrum is the same as in the case of no spin-orbit coupling, the latter interaction causing relatively small additional splitting of vibronic levels. This splitting is maximally pronounced in *unique* levels, where it is roughly equal to the value of A_{SO} , and almost negligible in non-*unique* levels. The vibronic wave functions remain nearly the same as in the case $A_{SO} = 0$; the only qualitative difference concerns the $K = 0, S_z' = \pm 1$ vibronic states, the wave functions of which cannot be classified exactly into Σ^+ and Σ^- species according to behavior upon reflections in the symmetry planes.

When the vibronic and spin-orbit coupling are comparable strong, as in the case of the $A^3\Pi_u$ electronic state of NCN (actually, although the quantities $\varepsilon\omega_2$ and A_{SO} for this state are of the same order of magnitude, the former is roughly by a factor of three larger than the latter), the coarse structure of the part of the vibronic spectrum corresponding to a particular ν_2 quantum number is determined by the relatively large energetic separation of the *unique* level from its non-*unique* counterparts, relatively large spin-orbit splitting of the former, and small splitting of the latter ones. While the wave functions for the non-*unique* P

$=K$ (i.e., $S_z'=0$) vibronic levels are represented by linear combinations of the $|\Lambda=1, \nu_2, l=K-1, S_z'=0\rangle$ and $|\Lambda=-1, \nu_2, l=K+1, S_z'=0\rangle$ basis functions with expansion coefficients of nearly (for $K=0$, of exactly) equal magnitude, the magnitudes of these coefficients differ considerably from each other for the $S_z'=\pm 1$ cases, this difference becoming continuously larger with increasing ratio $|A_{SO}/\epsilon\omega|$.

TABLE IV. Vibronic spectrum in the ${}^3\Pi_u$ electronic state of a triatomic molecule, computed variationally employing the following parameters: V^+ (in *hartree*) = $V^- = 0.0614 \rho^2 + 0.009 \rho^4$, $A_{SO} = -37 \text{ cm}^{-1}$, the kinetic energy operator for infinitesimal bending vibrations ($\mu = 11.3819$). For key to notation see also Table I

K	ν_2	$S_z' = -1$	$S_z' = 0$	$S_z' = 1$
0	1	1035.52	1072.52	1035.52
	1	1109.52	1072.52	1109.52
	3	2117.12	2154.11	2117.12
	3	2191.11	2154.11	2191.11
	5	3207.59	3244.59	3207.59
	5	3281.59	3244.59	3281.59
1	0	572.49	535.49	498.50
	2	1574.05	1611.05	1575.57
	2	1649.57	1612.57	1648.05
	4	2660.13	2697.12	2661.63
	4	2735.63	2698.63	2734.13
2	1	1109.52	1072.52	1035.52
	3	2114.09	2151.09	2117.12
	3	2191.11	2154.11	2188.09
	5	3204.60	3241.60	3207.59
	5	3281.59	3244.59	3278.60
3	2	1648.05	1611.05	1574.05
	4	2655.62	2692.62	2660.13
	4	2734.13	2697.12	2729.62
4	3	2188.09	2151.09	2114.09
	5	3198.63	3235.63	3204.60
	5	3278.60	3241.60	3272.63

The last two points of our analysis concern the effects of anharmonicity of the bending potentials and replacement of the kinetic energy operator for infinitesimal vibrations by its counterpart allowing for a reliable description of large amplitude bendings. They always influence quantitatively the vibronic energy terms, but there are situations where the anharmonicity and kinetic energy effects also change qualitatively the vibronic energy pattern. This happens when the splitting of the potentials upon bending is negligible, as it was found for example in the $X^5\Delta_g$ state of FeH_2 . Very weak splitting of the components of spatially degenerate electronic states is expected particularly in electronic states with larger Λ values, because the magnitude of the splitting depends for small deviations from linearity on $\rho^{2\Lambda}$.²³ In Table

IV are given the vibronic levels obtained in calculations in which the adiabatic potentials for 1^3A_1 and 2^3B_1 electronic states are assumed to be of the same form (*i.e.*, not split from each other) and slightly anharmonic; the zeroth-order kinetic energy operator T_0 is employed. Comparison of these results with their counterparts from Table III (vibronic energies without parentheses), generated in computations in which the harmonic (unsplit) potentials are used, shows that the systematic degeneracy of the latter vibronic levels is partly lifted and the positions of all vibronic levels are slightly changed as a consequence of the anharmonicity of the potentials. In the absence of splitting of the bending potentials curves, all vibronic states with a particular K value fall into two distinct groups: in the first one are those built from the basis functions labelled by the quantum number $l = K - 1$, in the second one only the $l = K + 1$ basis functions are involved. Thus the calculation of K vibronic levels in a Π electronic state with unsplit bending potentials is equivalent to the calculation of $l = K - 1$ and $l = K + 1$ levels in a Σ electronic state with the same bending potential. Under the effect of anharmonicity, the energies of the levels with the same ν_2 but different l values are not equal (being the case when anharmonicity is absent); a quartic order anharmonicity with a positive sign (the present case) causes the energy of all levels to increase, being more pronounced for levels with smaller l quantum numbers. Since the $K = 0$ vibronic levels correspond to $l = +1$ and $l = -1$ bending levels remain degenerate (for a given ν_2) also in the case of anharmonicity, the $K = 0$ levels are doubly degenerate even if anharmonicity is introduced. On the other hand, the double degeneracy of $K \neq 0$ levels is lifted, because one number of each pair corresponds to the $l = K - 1$ and the other to the $l = K + 1$ level. The $l = K + 1$ component of a K vibronic levels has the same energy as the $l = K' - 1$ component of the $K' = K + 2$ level corresponding to the same ν_2 quantum number. Let us illustrate that on the example of $\nu_2 = 5$ ($S_z = 0$) vibronic levels from Table IV: There are two $K = 0$ levels of the same energy, 3244.59 cm^{-1} , corresponding to $l = +1$ and $l = -1$ bending levels of the Σ electronic state with the same potential. The $K = 2$ levels with the same ν_2 have the energies of 3241.60 ($l = 3$) and 3244.59 ($l = 1$). The only (*unique*, $l = 3$) $K = 4$ vibronic level corresponding to $\nu_2 = 5$ possess an energy of 3241.60 cm^{-1} , the same as its $K = 2$, $l = 3$ counterpart.

Replacement of the kinetic energy operator for infinitesimal vibrations by its large-amplitude bending counterpart has the same qualitative effect concerning the removal of degeneracy as the anharmonicity of the potential (see Table III, vibronic term values in parentheses). The difference in our case is that the vibronic energies are now shifted downwards and that the $l = K - 1$ levels lie below their $l = K + 1$ counterparts. This kinetic energy effect is thus quite equivalent to the effect of negative anharmonicity of the potentials.

CONCLUSION

The interplay between the vibronic and spin-orbit couplings in the $^3\Pi$ electronic states of triatomic molecules has been little studied so far. In this paper the results of a systematic study of the various effects determining the structure of such spectra are presented. As a concrete example was chosen the $A^3\Pi$ state of the NCN radical. Both the *ab initio* computed and the experimentally derived parameters (potential energy curves, spin-orbit constant, equilibrium geometry) are employed in variational and perturbative calculation carried out at various levels of sophistication.

ИЗВОД

КОМБИНАЦИЈА ВИБРОНСКЕ И СПИН-ОРБИТНЕ СПРЕГЕ У $^3\Pi$ СТАЊИМА
ТРИАТОМСКИХ МОЛЕКУЛА НА ПРИМЕРУ $A^3\Pi_u$ ЕЛЕКТРОНСКОГ СТАЊА NCN

МАРИЈА КРМАР и МИЉЕНКО ПЕРИЋ

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Систематски је студиран утицај различитих ефеката на структуру спектра линеарних триатомских молекула у $^3\Pi$ електронским стањима. Посебна пажња посвећена је комбинацији вибронске и спин-орбитне спреге. Извршена су варијациона и пертурбациона рачунања на различитим нивоима софистикације за $A^3\Pi_u$ стање радикала NCN .

(Примљено 7. маја 2001)

REFERENCES

1. M. Born, R. J. Oppenheimer, *Ann. Physik* **84** (1927) 457
2. R. Renner, *Z. Phys.* **92** (1934) 172
3. M. Perić, B. Ostojić, J. Radić-Perić, *Phys. Rep.* **290** (1997) 283
4. M. Perić, S. D. Peyerimhoff, R. J. Buenker, *Int. Rev. Phys. Chem.* **4** (1985) 85
5. M. Perić, B. Engels, S. D. Peyerimhoff, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, S. R. Langhoff, Ed. Kluwer, Dordrecht, The Netherlands, 1995, p. 261
6. H. Martini, C. M. Marian, M. Perić, *Mol. Phys.* **95** (1998) 27
7. M. Perić, *Chem. Phys. Lett.* **301** (1999) 73
8. M. Perić, M. Krmar, J. Radić-Perić, M. Hanrath, *J. Mol. Spectrosc.* **204** (2000) 226
9. M. Perić, M. Krmar, J. Radić-Perić, Lj. Stevanović, *J. Mol. Spectrosc.* submitted
10. K. R. Jennings, J. W. Linnett, *Trans. Faraday Soc.* **56** (1960) 1737
11. G. Herzberg, D. N. Travis, *Can. J. Phys.* **42** (1964) 1658
12. D. McNaughton, G. F. Metha, R. Tay, *Chem. Phys.* **198** (1995) 107
13. K. D. Hensel, J. M. Brown, *J. Mol. Spectrosc.* **180** (1996) 170
14. M. Wienkoop, W. Urban, J. M. Brown, *J. Mol. Spectrosc.* **185** (1997) 185
15. S. A. Beaton, Y. Ito, J. M. Brown, *J. Mol. Spectrosc.* **178** (1996) 99
16. S. A. Beaton, J. M. Brown, *J. Mol. Spectrosc.* **183** (1997) 347
17. P. Rajendra, P. Chandra, *J. Chem. Phys.* **114** (2000) 1589
18. T. H. Dunning Jr., *J. Chem. Phys.* **90** (1988) 1007
19. *MOLCAS Version 4*, K. Andersson, M. R. A. Blomberg, M. P. Fuelscher, G. Karlstroem, R. Lindh, P.-Å. Malmqvist, P. Neogady, J. Olsen, B. O. Roos, A. J. Sadlej, M. Schuetz, L. Seijo, L. Serrano-Andres, P. E. M. Siegbahn, P.-O. Widmark, Lund University, Sweden (1997)
20. M. Hanrath, B. Engels, *Chem. Phys.* **225** (1997) 197
21. R. J. Buenker, S. D. Peyerimhoff, *Theoret. Chim. Acta* **35** (1974) 33; **39** (1974) 217; R. J. Buenker, S. D. Peyerimhoff, W. Butscher, *Mol. Phys.* **35** (1978) 771; R. J. Buenker, R. A. Phillips, *J. Mol. Struct.* **123** (1985) 291
22. S. R. Langhoff, E. R. Davidson, *Int. J. Quantum Chem.* **8** (1974) 61
23. J. M. Brown, F. Jorgensen, in *Advances in Chemical Physics*, I. Prigogine and S. A. Rice, Eds., Vol 52, p. 117, Wiley, New York, 1984
24. J. T. Hougen, P. R. Bunker, J. W. C. Johns, *J. Mol. Spectrosc.* **34** (1970) 136
25. J. A. Pople, *Mol. Phys.* **3** (1960) 16
26. J. T. Hougen, *J. Chem. Phys.* **36** (1962) 519
27. G. Herzberg, *Molecular Spectra and Molecular Structure III. Electronic Spectra of Polyatomic Molecules*, Van Nostrand, New York, 1967
28. A. J. Merer, D. N. Travis, *Can. J. Phys.* **43** (1965) 1795.