CALCULATIONS OF QUARTET STATE SPECTRA FOR DIATOMIC SPECIES BY INDO CI METHOD INCLUDING SPIN-ORBIT COUPLING PERTURBATION

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In memorial to Dr V. Čermák, the founder of electron spectroscopy of Penning ionization.

Transition dipole moments for quartet-doublet transitions in diatomic species (NO, O_2^+ and CF) have been calculated on the basis of the INDO CI method and spin-orbit coupling (SOC) has been taken into account as a perturbation. Qualitative description of the first excited quartet and doublet states and occurrence of quartet states in photoelectron spectra are briefly discussed. The intensity and polarization of the components of the $a^4\Pi - X^2\Pi$ transitions in NO and O_2^+ and the $a^4\Sigma^- - X^2\Pi$ transition in CF have been calculated. Fine structure constants (SOC constant A for $^2\Pi$ and $^4\Pi$ states, spin-rotation and zero-field splitting for the $^4\Sigma^-$ state) have been obtained and compared with experiment where possible.

While the doublet excited state spectra of many diatomic radicals are rather well understood[1], information on the quartet states and especially on the doublet-quartet transitions is scarce.

It is possible to observe the quartet states of radical cations, corresponding to parent molecules with triplet ground state, in photoelectron spectra (PES). This is because the intensity of the different ion states appearing in PES, follows in general the rules given by Price[2], according to which the intensity of different states, originating from the same electronic configuration, is directly proportional to their multiplicities. Therefore, the relative transition probabilities to doublet and quartet states of the same electronic configuration in PES are 1 : 2. A well known example is O_2 (ref.[3]). The same applies to PES for NH, NCN, CH_2 *etc.*

On the other hand, it is very difficult to observe quartet states in optical spectra because the ground states of great variety of diatomic species, with an odd number of electrons, are doublets** and doublet-quartet electronic transitions are forbidden by the spin selection rule.

Although the quantum chemical calculations identify the quartet state as the first excited valence state for numerous diatomic species[4], there are only few observations of optical quartet-doublet transition concerning emission of the NO radical in solid matrices of rare gases[7,8] and of the SiF and GeF radicals in gase phase[9,10].

A simple classification of ground and first excited valence states for first row diatomic species is presented in Fig. 1.

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[**] There are some exceptions: C_2^+ (ref.[4,5]), and transition metal containing diatomic species like MnH, MnF, MnCl, MnBr, MnI, FeCl (ref.[1]), CoO, MoN, NbO (ref.[6]).

It is easy to see from the simple MO picture (Fig. 1) and also from proper CI calculations (semiempirical[4] and *ab initio*[5,11-14]) that quartet states are the first (lowest lying) excited valence states in the systems with $N = 5$ for X—H hydrides, and with $N = 11$ for X—Y biatomics (N is the number of valence electrons), *e.g.*, in CH, NH^+, CF, NO, O_2^+. By analogy it is possible to predict that the same picture should hold for the second row diatomics, *e.g.*, SiH, PH^+, SiF, CCl, SiCl, PO, NS, PS, SO^+, S_2^+.* The $a^4\Sigma^-$ state of SiF is the most investigated case, because of many works devoted to the rotational analysis of the $a^4\Sigma^- - X^2\Pi$ transiton[9,10,16]. There is some experimental evidence for a very low-lying $a^4\Sigma^-$ state in NH^+ from perturbations it causes in the ground $X^2\Pi$ state[17], and for the first excited $a^4\Pi$ states in NO (from optical emission[7,8] and electron-impact excitation[18]) and in O_2^+ from PES (ref.[3]). For other first row radicals (CH, CF) the quartet states have not yet been observed.

Quartet states can also manifest themselves in electronic quartet-quartet optical transitions Herzberg[1] reported only two transitions involving quartet states, $b^4\Sigma_g^- - a^4\Pi_u$ transition in O_2^+ and a possible $^4\Pi - {}^4\Sigma$ transition in FeCl. Many other transitions of this sort have been reported[6,7,19] in recent years.

In this article we shall discuss manifestations of quartet state properties in PES and optical spectra (with special attention to doublet-quartet transitions within the first row diatomic species, mentioned above) on the basis of INDO CI wave functions. The INDO CI calculations were published earlier and provided a realistic state ordering in radicals with the degenerate ground state[4].

Perturbation Treatment for the D – Q Transitions

The transition probability of the multiplicity forbidden $^4\Psi_1 - {}^2\Psi_0$ transition depends on the doublet character of $^4\Psi_1$ and the quartet character of $^2\Psi_0$, which can be estimated by treating the spin-orbit coupling (SOC) by means of perturbation theory:

$$^4\tilde{\Psi}_1 = {}^4\Psi_1 + \sum_n \frac{\langle {}^2\Psi_n | \mathbf{H}_{SO} | {}^4\Psi_1 \rangle}{^4E_1 - {}^2E_n} \, {}^2\Psi_n \tag{1}$$

$$^2\tilde{\Psi}_0 = {}^2\Psi_0 + \sum_p \frac{\langle {}^4\Psi_p | \mathbf{H}_{SO} | {}^2\Psi_0 \rangle}{^2E_0 - {}^4E_p} \, {}^4\Psi_p \, . \tag{2}$$

The dipole transition moment for $^2\Psi_0 - {}^4\Psi_1$ optical excitation or emission is, therefore, as follows:

$$\langle {}^2\Psi_0 | e \sum_i r_i | {}^4\Psi_1 \rangle = \sum_n \frac{\langle {}^2\Psi_n | \mathbf{H}_{SO} | {}^4\Psi_1 \rangle}{^4E_1 - {}^2E_n} \langle {}^2\Psi_0 | e \sum_i r_i | {}^2\Psi_n \rangle + {} + \sum_p \frac{(\langle {}^4\Psi_p | \mathbf{H}_{SO} | {}^2\Psi_0 \rangle)^+}{^2E_0 - {}^4E_p} \langle {}^4\Psi_p | e \sum_i r_i | {}^4\Psi_1 \rangle \, . \tag{3}$$

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* This prediction coincides with the *ab initio* results[15], obtained for PO, NS, SiF and CCl radicals.

It obviously follows that

$$(\langle {}^4\Psi_p|\mathbf{H}_{\mathrm{SO}}|\,{}^2\Psi_0\rangle)^+ = \langle {}^2\Psi_0|\mathbf{H}_{\mathrm{SO}}|\,{}^4\Psi_p\rangle\,. \tag{4}$$

If $n = 0$ and $p = 1$, we obtain a special contribution from the permanent electric dipole moment:

$$\frac{\langle {}^2\Psi_0|\mathbf{H}_{\mathrm{SO}}|\,{}^4\Psi_i\rangle}{{}^4E_1 - {}^2E_0}\,{}^2\mu_0 + \frac{\langle {}^2\Psi_0|\mathbf{H}_{\mathrm{SO}}|\,{}^4\Psi_1\rangle}{{}^2E_0 - {}^4E_1}\,{}^4\mu_1 = \frac{\langle {}^2\Psi_0|\mathbf{H}_{\mathrm{SO}}|\,{}^4\Psi_1\rangle}{{}^4E_1 - {}^2E_0}\,({}^2\mu_0 - {}^4\mu_1)\,, \tag{5}$$

where ${}^2\mu_0 = \langle {}^2\Psi_0|e\sum_i r_i|\,{}^2\Psi_0\rangle$ is a ground state permanent electric dipole moment. Obviously SOC of the doubletground and first excited quartet states contributes to the ${}^2\Psi_0 - {}^4\Psi_1$ transition intensity *via* the difference between permanent dipole moments in the ground and upper states. As the completed calculations show, the last contribution is often very important. Taking into account Eqs (*4*) and (*5*) and using selfex-

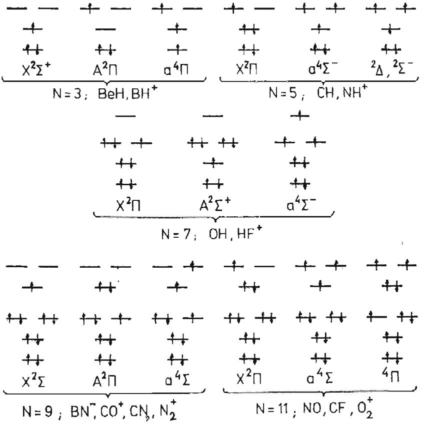

FIG. 1

Orbital Diagrams of First Row Diatomic Radicals of Various Types
N is the number of valence electrons.

planatory abreviations, expression (*3*) assumes the form:

$$\langle {}^2\Psi_0|\mu|\,{}^4\Psi_1\rangle = \sum_n c_{n1}\,{}^2\mu_{01} - \sum_p c_{0p}\,{}^4\mu_{p1}\,. \qquad (6)$$

Calculations of ${}^4\Psi_1 - {}^2\Psi_0$ transition probabilities require a knowledge of energies for all states that can mix with the ${}^4\Psi_1$ and ${}^2\Psi_0$ states by SOC and the transition moments of the corresponding allowed quartet-quartet and doublet-doublet transitions from which ${}^4\Psi_1 - {}^2\Psi_0$ transition probability is borrowed. As the calculated ${}^4\Psi_1 - {}^2\Psi_0$ transition probabilities depend rather dramatically on the energy values, some experimental state energies will be used for comparison.

Occurrence of Quartet States in PES

An investigation of relative intensities in PES, for the cation states possessing the same electronic configuration[20,21], represents a very good test of quality for CI wave functions. Let us first deal with the O_2^+ cation. The PES of molecular oxygen[3,20,21] and electronic spectrum of O_2^+ (ref.[1]) yield a great deal of detailed information about the low-lying electronic states of the cation. The CI between the ${}^2\Pi_u$ states of the O_2^+ ion leads to a correct prediction of relative intensities of peaks in PES of $O_2({}^3\Sigma_g^-)$[20] and metastable $O_2({}^1\Delta_g)$ (ref.[21]) states (including relative intensities of transitions to the ${}^2\Phi_u$ and ${}^2\Pi_u$ states from the $\sigma_g^2\pi_u^2\pi_g^2$ configuration[21]). It is very important for our purposes that the quartet states are well established from the PES measurements. This information can be used to study and predict optical doublet-quartet transition properties. The calculated INDO CI relative peak intensities in the PES of O_2 are compared in Table I with the *ab initio* predictions[20,21] and experiment[14]. The ratio of the photocurrents belonging to the $a^4\Pi_u$ and $A^2\Pi_u$ states of O_2^+, obtained in our and other calculations[20,21], is approximately 2 : 0·4, rather than that corresponding to the statistical ratio of 2 : 1, which explains the absence of significant ionization to the first excited doublet state, $A^2\Pi_u$, with 21·21 eV photons. The photocurrent in a broad peak at about 23·7 eV obtained with 40·81 eV photons is about one third of that for the $a^4\Pi_u$ state, and was assigned to the upper ${}^2\Pi_u$ state[20]. All calculations[4,20,21] support this assignment. Clearly, the present calculation of relative intensities of photocurrents and energies in PES of $O_2({}^3\Sigma_g^-)$, based on semiempirical INDO CI wave function is very close to the *ab initio* results[21] (Table I).

In the case of closed shell ground state of the parent molecule, PES transitions to quartet states of the respective cation are forbidden. However, when SOC is taken into account, these transitions become slightly allowed. For example, the first broad diffuse band in PES of N_2O can be tentatively assigned to the $a^4\Pi$ state of N_2O^+ (ref.[4,22]). Using the INDO CI wave functions, mixing of the $a^4\Pi$ state with the $X^2\Pi$ state of N_2O^+ has been calculated with the following result: $\langle X^2\Pi|\mathbf{H}_{SO}|\,a^4\Pi\rangle = -21{\cdot}4\ \text{cm}^{-1}$, $c_{01} = -21{\cdot}4/11400 \simeq 2 \times 10^{-3}$. Therefore the intensity of the

$^4\Pi$ band ought to be weaker by five-six orders of magnitude than the intensity of the first intense peak ($X^2\Pi$) in PES of N_2O.

SOC Constants and Doublet-Quartet Transition Probabilities in Isoelectronic Radicals CF, NO, O_2^+

It has been shown[23,24] that the zero differential overlap approximation is rather good for calculations of SOC matrix elements. In this approximation the SOC operator assumes the form[23]:

$$\mathbf{H}_{SO} = \sum_A \zeta_A \sum_i \mathbf{l}_{iA}\mathbf{s}_i = \sum_i \mathbf{B}_i \mathbf{s}_i \,, \tag{7}$$

where ζ_A is a SOC constant for valence shell electrons of the atom A, and $\mathbf{l}_{iA}$ and $\mathbf{s}_i$ are orbital and spin angular momentum operators, expressed in $\hbar$ units, for the i-th

TABLE I

Relative Transition PES Probabilities from O_2 ($^3\Sigma_g^-$) to the $|^4\Pi_u\rangle$, $|^2\Pi_u, 1\rangle$, $|^2\Pi_u, 2\rangle$, $|^2\Pi_u, 3\rangle$ States of O_2^+

$\lvert ^4\Pi_u\rangle$	$\lvert ^2\Pi_u, 1\rangle$	$\lvert ^2\Pi_u, 2\rangle$	$\lvert ^2\Pi_u, 3\rangle$	Origin
2	0·41	0·02	0·54	this work
2	0·37	0·02	0·54	*ab initio*[21]
2	0·34	0·001	0·64	semiempirical CI (ref.[20])
2	—	—	0·66	experiment[3]

TABLE II

RHF INDO Valence Orbital Energies (eV)

$C_{\infty v}$	CF	NO	O_2^+
3σ	—48·63	—48·80	—64·53
4σ	—21·79	—21·64	—33·15
1π	—17·49	—16·25	—26·92
5σ	—14·10	—14·96	—26·33
2π	—2·21	—2·56	—12·56
6σ	10·25	13·43	7·47

electron. Formula (7) has proved rather useful in CNDO interpretations of a variety of properties depending on SOC in molecules[25,26]. In this approximation the SOC constant for multiplet splitting, A, ($W = A\Lambda\Sigma^1$), is equal, for example for the $\sigma^2\pi$ configuration ($^2\Pi_r$), to $A(^2\Pi_r) = \sum_A (C_\pi^A)^2 \zeta_A = B_{\pi\pi}$, where C_π^A is the LCAO expansion coefficient of π-MO, and for $\sigma^2\pi^3$ configuration is equal to $A(^2\Pi_i) = -B_{\pi\pi}$[24].

We shall deal now with the isoelectronic series of radicals, CF, NO, O_2^+. Energies of MO's, obtained by restricted Hartree-Fock (RHF) half electron method[27] in INDO approximation[4] are given in Table II. Some configurations having spectroscopic importance are presented in Table III. Description of the CI procedure and types of D^α, D^β, A configurations are available in ref.[28]. CI between the three $^2\Pi$ configurations (D^α, D^β, A) is of great importance in connection with the SOC constants for these $^2\Pi$ states[12-14,29]. For the O_2^+ ion the CI mixing is also important for PES intensities as mentioned above. SOC constants for $^{2S+1}\Pi$ multiplets calculated by these CI wavefunctions are given in Table IV. Agreement with experiment is not

TABLE III

The Most Important Configurations for CF, NO and O_2^+ Radicals

... $1\pi^4\ 5\sigma^2\ 2\pi$; $X^2\Pi$ Ground state
... $1\pi^4\ 5\sigma\ 2\pi^2$; $^4\Sigma^-$, $^2\Delta$, $^2\Sigma^+$, $^2\Sigma^-$
... $1\pi^3\ 5\sigma^2\ 2\pi^2$; $^4\Pi$, $^2\Phi$, three $^2\Pi(D^\beta, D^\alpha + A)$

TABLE IV

SOC Constants for $^{2S+1}\Pi$ Multiplets in the Isoelectronic Series of CF, NO and O_2^+

$^{2S+1}\Pi$	CF			NO			O_2^+		
	this work	*ab initio* (ref.[12])	exp. (ref.[32])	this work	*ab initio*[a] (refs[13,29])	exp. (ref.[29])	this work[b]	*ab initio*[a] (ref.[33])	exp. (ref.[1])
$X^2\Pi$	53·5	78·6	77·1	100·5	146	124	159	191	195
$^4\Pi$	—82·1			—41·2	—36[a]	—20	—53	—49	—48
$^2\Pi$, 1	138·3			46·1	31	33	53	48	8·2

[a] Calculated from *ab initio* wavefunction with the semiempirical treatment of SOC (ref.[29]); [b] Atomic SOC constant, ξ_0, for cation determined in the manner described in refs[23,24].

very good, but its qualitative features are reproduced*. The NDO approximation underestimates the SOC constants for antibonding π MO, and overestimates them for bonding π MO.

The B_{ij} integrals based on MO needed for evaluation of SOC matrix elements are given in Table V. For the sake of comparison these integrals for the NO radical, based on *ab initio* calculations, are as follows: $B_{1\pi,1\pi} = 93\,\text{cm}^{-1}, B_{2\pi,2\pi} = 146\,\text{cm}^{-1}$ (ref.[13]), $B_{1\pi,5\sigma} = 50\,\text{cm}^{-1}$, $B_{2\pi,5\sigma} = 152\,\text{cm}^{-1}$ (private communication from H. Lefebvre-Brion cited in ref.[30]).

Let us deal now with the $X^2\Pi - {}^4\Pi$ transition probabilities for our series, *i.e.* with the first optical excitation in the NO and O_2^+ radicals. Contributions to the transition moment are determined by the following matrix elements:

$$\begin{aligned} \langle X^2\Pi_{3/2}|\mathbf{H}_{\text{SO}}|\,{}^4\Sigma^-_{3/2}\rangle &= \frac{1}{2}\,B_{2\pi,5\sigma} \\ \langle X^2\Pi_{1/2}|\mathbf{H}_{\text{SO}}|\,{}^4\Sigma^-_{1/2}\rangle &= \frac{1}{\sqrt{12}}\,B_{2\pi,5\sigma} \end{aligned} \tag{8}$$

$$\langle X^2\Pi_{1/2}|\mathbf{H}_{\text{SO}}|\,{}^4\Pi_{1/2}\rangle = \langle X^2\Pi_{3/2}|\mathbf{H}_{\text{SO}}|\,{}^4\Pi_{3/2}\rangle = \frac{1}{\sqrt{3}}\,B_{1\pi,2\pi} \tag{9}$$

$$\begin{aligned} \langle {}^2\Sigma^-_{1/2}|\mathbf{H}_{\text{SO}}|\,{}^4\Pi_{1/2}\rangle &= \frac{1}{3\sqrt{2}}\,B_{1\pi,5\sigma} \\ \langle {}^2\Sigma^-_{1/2}|\mathbf{H}_{\text{SO}}|\,{}^4\Pi_{-1/2}\rangle &= \frac{1}{\sqrt{6}}\,B_{1\pi,5\sigma}\,. \end{aligned} \tag{10}$$

In these matrix elements we neglect very small CI contributions from the 3σ and 4σ MO. For example, in NO the first integral (*10*) assumes the form: $1/3\sqrt{2}$ $(0{\cdot}9985B_{1\pi,5\sigma} + 0{\cdot}04B_{1\pi,4\sigma} + 0{\cdot}037B_{1\pi,3\sigma})$. Formulae (*8*) and (*10*) coincide with the results of ref.[29]. For the $X^2\Pi - {}^4\Pi$ transition, integrals (*8*) determine intensity borrowing from the ${}^4\Pi - {}^4\Sigma^-$ transition, integrals (*10*) from the $X^2\Pi - {}^2\Sigma^-$ transition, and integrals (*9*) from the difference of the permanent dipole moments, ${}^2\mu_0 - {}^4\mu_1$. The same type of intensity borrowing, like the last source, (polarization of the transition is parallel to interatomic axes) is determined by SOC between the

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* In the CF radical the π-shell is highly polarized. The 1π MO is located predominantly on the F atom, and the 2π MO on the C atom. SOC constants for the ${}^2\Pi$ states depend heavily on this balance. INDO wavefunction for the 2π MO has the form: $\varphi_{2\pi} = -0{\cdot}95\chi^C_\pi + 0{\cdot}313\chi^F_\pi$. If it were slightly changed to the form $\varphi'_{2\pi} = -0{\cdot}9\chi^C_\pi + 0{\cdot}436\chi^F_\pi$, the SOC constant for the $X^2\Pi$ state would coincide with experiment.

$^4\Pi$ state and the excited $^2\Pi,n$ ($n = 1, 2, 3$) states (Table VI). There are no simple expressions available for these SOC matrix elements, because they depend on CI mixing among the $^2\Pi$ configuration of the A, D^α and D^β types. The last far UV transition to the $^2\Pi,3$ state is extremely intense for the NO and O_2^+ radicals, but its contribution to the intensity of the $X^2\Pi - a^4\Pi$ transition is relatively small because of the negligible SOC mixing of the $a^4\Pi$ and $^2\Pi,3$ states. All results of the perturbation theory calculations (*1*)–(*6*) are summarized in Tables VI and VII. Results of the third transition in Table VII have to be considered simultaneously with the results of Table VI. The total values of the transition dipole moments, $\langle X^2\Pi_\Omega|\mu|\,^4\Pi_\Omega\rangle$, for the NO, O_2^+ and CF radicals are $-2{\cdot}72 \times 10^{-3}$, $-3{\cdot}93 \times 10^{-3}$ and $-4{\cdot}3 \times 10^{-3}$, respectively. These transitions correspond to $\Omega = 1/2$ or $3/2$ and are labelled by numbers 3 and 3′ in Fig. 2. Intensities for all other spin-orbit allowed transitions between spin sublevels of the ground $X^2\Pi_r$ and the upper $^4\Pi_i$ states, indicated in Fig. 2, can be obtained from Table VII. Numbers of transitions are given in the first column of Table VII.

Emission of the NO radical (trapped in a solid rare gas matrix and initiated by X-rays) was tentatively assigned to the $a^4\Pi_{5/2} \rightarrow X^2\Pi_{3/2}$ transition (referred to as the M band)[7,8]. Since the emitting quartet state has a long lifetime ($\tau = 0{\cdot}16$, $0{\cdot}09$ and $0{\cdot}03$ s in solid Ne, Ar and Kr, respectively), it is reasonable to assume that

TABLE V

SOC Integrals, B_{ij}, Calculated by the INDO Method (cm^{-1})

AB	a_1 $B_{1\pi,1\pi}$	a_2 $B_{2\pi,2\pi}$	a_3 $B_{1\pi,5\sigma}$	a_4 $B_{2\pi,5\sigma}$	a_5 $B_{1\pi,2\pi}$
CF	246·4	53·5	100·0	50·4	71·4
O_2^+	159	159	0	135	0
NO	123·5	100·5	42·4	88·0	37·3

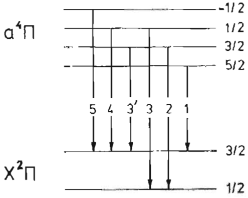

FIG. 2

Designation of Transitions between Spin Sublevels for the $a^4\Pi - X^2\Pi$ Transition (NO, O_2^+)

TABLE VI

Contributions from the $X^2\Pi - {}^2\Pi, n(1-3)$ Transitions to the $\langle X^2\Pi_\Omega|\mu_\parallel|\,{}^4\Pi_\Omega\rangle$ Dipole Transition Moment ($\Omega = 1/2$ or $3/2$)

	$\langle {}^4\Pi_\Omega|\mathbf{H}_{SO}|\,{}^2\Pi_\Omega, n\rangle$ cm^{-1}			$\langle X^2\Pi_\Omega|\mu_\parallel|\,{}^2\Pi, n\rangle^a$ $\times 10^{30}$ Cm			$E({}^4\Pi) - E({}^2\Pi, n)$ $\times 10^{-3}$ cm^{-1}			$\langle X^2\Pi_\Omega|\mu_\parallel|\,{}^4\Pi_\Omega, n\rangle$ $\times 10^{34}$ Cm			$\sum_n \mu_n$ $\times 10^{34}$ Cm
n:	1	2	3	1	2	3	1	2	3	1	2	3	
CF	—87·3	—60·2	—64·3	0·944	—1·348	—6·364	—5·4	17·3	—27·3	152·40	—48·07	—149·97	—45·60
NO	—54·7	—83·2	—7·9	—0·527	—0·700	—11·891	—11·9	27·0	—67·2	—24·28	—21·61	—13·98	—59·84
O_2^+	—76·5	—122·7	0·9	—0·830	—0·974	—13·089	—7·5	—24·7	—74·3	—84·66	—48·20	1·60	—131·25

[a] Result for one component of the multiplet. The negative dipole sign is assigned to the $\overset{(+)}{C}$—$\overset{(-)}{F}$ polarization.

TABLE VII

Contributions to the $\langle X^2\Pi_\Omega|\mu|\,^4\Pi_{\Omega'}\rangle$ Dipole Transition Moments Originating from SOC Mixing

Number of transition	Radical	cm^{-1}	10^{30} Cm	$10^{-3}\ \mathrm{cm}^{-1}$	10^{34} Cm
		$\langle X^2\Pi_{3/2}\|\mathbf{H}_{\mathrm{SO}}\|\,^4\Sigma^-_{3/2}\rangle$	$\langle ^4\Pi_{5/2}\|\mu_\perp\|\,^4\Sigma^-_{3/2}\rangle^{a,b}$	ΔE	$\langle X^2\Pi_{3/2}\|\mu_\perp\|\,^4\Pi_{5/2}\rangle$
1	CF	25·2	—1·834	24·7	—18·75
	NO	44	—2·802	46·0^c	—26·78
	O_2^+	67·5	—2·822	45·6	—41·76
		$\langle X^2\Pi_{1/2}\|\mathbf{H}_{\mathrm{SO}}\|\,^4\Sigma^-_{1/2}\rangle$	$\langle ^4\Pi_{3/2}\|\mu_\perp\|\,^4\Sigma^-_{1/2}\rangle$		$\langle X^2\Pi_{1/2}\|\mu_\perp\|\,^4\Pi_{3/2}\rangle$
2	CF	14·55	—1·834	24·7	—10·81
	NO	25·40	—2·802	46·0^c	—15·48
	O_2^+	38·97	—2·822	45·6	—24·12
		$\langle X^2\Pi_{1/2(3/2)}\|\mathbf{H}_{\mathrm{SO}}\|\,^4\Pi_{1/2(3/2)}\rangle$	$^2\mu_X - {}^4\mu_\Pi$		$\langle X^2\Pi_{1/2(3/2)}\|\mu_\parallel\|\,^4\Pi_{1/2(3/2)}\rangle$
3^d	CF	41·22	—16·40	69·1	—97·80
	NO	21·54	—5·43	38·0^c	—30·75
	O_2^+	0	0	42·5	0
		$\langle G^2\Sigma^-_{1/2}\|\mathbf{H}_{\mathrm{SO}}\|\,^4\Pi_{1/2}\rangle$	$\langle X^2\Pi_{3/2}\|\mu_\perp\|\,G^2\Sigma^-_{1/2}\rangle$		$\langle X^2\Pi_{3/2}\|\mu_\perp\|\,a^4\Pi_{1/2}\rangle$
4	CF	23·57	—5·927	45·9	—30·42
	NO	9·99	—1·707	—17·9^c	9·51
	O_2^+	0	0	—20·3	0
		$\langle G^2\Sigma^-_{1/2}\|\mathbf{H}_{\mathrm{SO}}\|\,^4\Pi_{-1/2}\rangle$	$\langle X^2\Pi_{3/2}\|\mu_\perp\|\,G^2\Sigma^-_{1/2}\rangle$		$\langle X^2\Pi_{3/2}\|\mu_\perp\|\,^4\Pi_{-1/2}\rangle$
5	CF	40·82	—5·927	45·9	—52·70
	NO	17·31	—1·707	—17·9	16·49
	O_2^+	0	0	—20·3	0

[a] The negative dipole sign is assigned to the C^+—F^- and N^+—O^- polarization; [b] $\mu_\parallel$ and $\mu_\perp$-parallel and perpendicular components of μ in the direction of molecular axes; [c] Experimental values for NO (ref.[18]); [d] To the No 3 transitions results of Table VI have to be added.

TABLE VIII

Contributions to the $a^4\Sigma^- - X^2\Pi$ Transition Dipole Moment of CF from the $X^2\Pi - {}^2\Pi, n$ Transitions

n	$\langle {}^2\Pi_{1/2}, n \vert \mathbf{H}_{SO} \vert a^4\Sigma^-_{1/2} \rangle$	$\langle X^2\Pi_{1/2} \vert \mu_{\Vert} \vert {}^2\Pi_{1/2}, n \rangle$	$E({}^4\Sigma^-) - E({}^2\Pi, n)$	$\langle X^2\Pi_{1/2} \vert \mu_{\Vert} \vert a^4\Sigma^-_{1/2} \rangle^a$
	cm^{-1}	10^{30} Cm	10^{-3} cm^{-1}	10^{34} Cm
1	17·21	0·9433	—58·94	—2·7542
2	4·75	—1·3833	—70·79	0·9283
3	18·05	—6·3657	—80·77	14·2257

[a] $\sum_{n} \mu_{\Pi,n} = 12{\cdot}4 \times 10^{-34}$ Cm.

there is ample time for establishing the Boltzmann equilibrium distribution over the spin sublevels[7]. At the given experimental conditions (4K)[7] the multiplet splitting was approximately an order of magnitude greater than kT and the only important emitter was the $^4\Pi_{5/2}$ sublevel. The oscillator strength of such an emission, estimated for our calculation, amounts to $1{\cdot}44 \times 10^{-8}$ and $\tau = 0{\cdot}07$ s. This result is rather similar to the prediction made in ref.[30]. Other theoretical estimations of the $a^4\Pi$ state radiative lifetime of NO (ref.[7,31]) are incorrect, as established in ref.[30].

Let us now consider the $a^4\Sigma^- - X^2\Pi$ transition in CF. Emission spectrum of CF, in a discharge through fluorocarbon vapours, has been investigated in the UV region by many authors[32] but there are no papers available on the region above 400 nm, where the $a^4\Sigma^- - X^2\Pi$ transition has been predicted on the basis of MO calculations[4,12].* In order to facilitate checking this prediction, intensity calculation for the $a^4\Sigma^- - X^2\Pi$ transition of CF have been performed. The results are as follows. Nonzero perpendicular components of the dipole transition moment amount to:**

$$\mu_1 = \langle X^2\Pi_{3/2}|\mu_\perp|\, a^4\Sigma^-_{1/2}\rangle = \frac{\langle X^2\Pi_{3/2}|\mathbf{H}_{\mathrm{SO}}|\, b^4\Pi_{3/2}\rangle}{E(^4\Pi) - E(X^2\Pi)}\,.$$

$$.\,\langle b^4\Pi_{3/2}|\mu_\perp|\, a^4\Sigma^-_{1/2}\rangle = \frac{41{\cdot}22\ \mathrm{cm}^{-1}}{78\,200\ \mathrm{cm}^{-1}}(-1{\cdot}838 \times 10^{-30}\ \mathrm{Cm}) =$$

$$= -9{\cdot}687 \times 10^{-34}\ \mathrm{Cm}$$

$$\mu_2 = \langle X^2\Pi_{1/2}|\mu_\perp|\, a^4\Sigma^-_{1/2}\rangle = \frac{\langle C^2\Sigma^+_{1/2}|\mathbf{H}_{\mathrm{SO}}|\, a^4\Sigma^-_{1/2}\rangle}{E(^4\Sigma^-) - E(C^2\Sigma^+)}\,.$$

$$.\,\langle X^2\Pi_{1/2}|\mu_\perp|\, C^2\Sigma^+_{1/2}\rangle = \frac{(-\sqrt{6}/3)\,B_{2\pi,2\pi}}{(24{\cdot}7-51{\cdot}7) \times 10^3\ \mathrm{cm}^{-1}}\,.$$

$$.\,3{\cdot}659 \times 10^{-30}\ \mathrm{Cm} = 5{\cdot}92 \times 10^{-33}\ \mathrm{Cm}\,.$$

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* A similar transition in SiF has been observed at 336 nm[10].

** Note that the transtition dipole moments for the $^2\Sigma^-$ states must be $\sqrt{3}$ times larger than for the $^2\Sigma^+$ state (both states possess $\sigma\pi^2$ configuration). Therefore the intensity of absorption from the $X^2\Pi$ ($\sigma^2\pi$) state to the $^2\Sigma^-$ state must be approximately three times larger than that to the $^2\Sigma^+$ state because frequency differencies for these transitions should be small. For every component of the $^2\Delta(\sigma\pi^2)$ states, transition dipole moment has the same value as for the $^2\Sigma^+$ state. Therefore the intensity of absorption transition to the $^2\Delta$ state must be approximately twice that to the $^2\Sigma^+$ state. INDO CI calculation show[4] that this simple theoretical rule is rather well obeyed by the CH, CF, NO, CCN and CNC radicals.

Nonzero parallel components consist of two contributions[+]: (*a*) the difference of the permanent dipole moments of the $X^2\Pi$ and $a^4\Sigma^-$ states, and, (*b*) to the dipole moment of the $X^2\Pi - {}^2\Pi$, n transitions.

(*a*)
$$\mu_3' = \langle X^2\Pi_{1/2}|\mu_{\|}|\, a^4\Sigma^-_{1/2}\rangle = \frac{\langle X^2\Pi_{1/2}|\mathbf{H}_{\mathrm{SO}}|\, a^4\Sigma^-_{1/2}\rangle}{E(^4\Sigma^-) - E(X^2\Pi)}\,.$$

$$.\,(^2\mu_0 - {}^4\mu_\Sigma) = \frac{14{\cdot}55\ \mathrm{cm}^{-1}}{24700\ \mathrm{cm}^{-1}}\,(-4{\cdot}486 \times 10^{-30}\ \mathrm{Cm}) = -2{\cdot}644 \times 10^{-33}\ \mathrm{Cm}$$

(*b*)
$$\mu_3'' = \langle X^2\Pi_{1/2}|\mu_{\|}|\, a^4\Sigma^-_{1/2}\rangle = \sum_{n=1}^{3} \frac{\langle {}^2\Pi_{1/2}, n|\mathbf{H}_{\mathrm{SO}}|\, a^4\Sigma^-_{1/2}\rangle}{E(^4\Sigma^-) - E(^2\Pi, n)}\,.$$

$$.\,\langle X^2\Pi_{1/2}|\mu_{\|}|\, {}^2\Pi_{1/2}, n\rangle$$

Results of calculations of the (*b*) contribution are summarized in Table VIII. From the last column of Table VIII $\mu_3'' = 1{\cdot}24 \times 10^{-33}$ Cm is obtained and the total transition moment $\mu_3 = \mu_3' + \mu_3'' = -1{\cdot}404 \times 10^{-33}$ Cm. The other nonzero parallel component of the transition dipole moment for the $\Omega = 3/2$ levels is determined by the expression

$$\mu_4 = \langle X^2\Pi_{3/2}|\mu_{\|}|\, a^4\Sigma^-_{3/2}\rangle = \sqrt{3}\langle X^2\Pi_{1/2}|\mu_{\|}|\, a^4\Sigma^-_{1/2}\rangle\,,$$

which originates from the SOC matrix elements (*8*). The numerical value for μ_4, $2{\cdot}432 \times 10^{-33}$ Cm, is obtained easily. For the intensity ratio of the perpendicular to the parallel polarization of the $a^4\Sigma^-_{1/2} - X^2\Pi_{1/2}$ emission for CF, there results

$$\left|\frac{\mu_{\|}}{\mu_{\perp}}\right|^2 = \left|\frac{\mu_2}{\mu_3}\right|^2 = 17{\cdot}8$$

Finally, the fine structure of the $a^4\Sigma^-$ state of CF will be considered. Obviously this state must be very close to the (*b*) case coupling. The rotational Hamiltonian assumes the form[9,16]:

$$\mathbf{H} = B(\mathbf{J} - \mathbf{L} - \mathbf{S})^2 + 2\lambda(\mathbf{S}_z^2 - \tfrac{1}{3}\mathbf{S}^2) + \gamma(\mathbf{J} - \mathbf{S})\mathbf{S}\,. \qquad (11)$$

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[*] It is easy to see that explanation of branch intensity in SiF (ref.[9]) is too simple. For example, authors of ref.[9] put μ_1 equal to zero, do not take into account μ_3'' and use rather crude "pure precession" hypothesis.

The terms in Eq. (*11*) have their usual meanings[9,16]. INDO CI calculation of spin-rotational coupling constant gives:*

$$\Delta g = \frac{2\langle a^4\Sigma^-_{1/2}|\mathbf{H}_{SO}|\, b^4\Pi_{-1/2}\rangle \langle b^4\Pi_{-1/2}|\mathbf{L}|\, a^4\Sigma^-_{1/2}\rangle}{E(a^4\Sigma^-) - E(b^4\Pi)} =$$

$$= \frac{-\frac{1}{3}(\sqrt{3})\, B_{1\pi,5\sigma}(-l_{5\sigma,1\pi})}{E(^4\Sigma^-) - E(^4\Pi)} = -0{\cdot}000234 \qquad (12)$$

$$\gamma = -2B\Delta g = +0{\cdot}000618\,, \qquad (13)$$

where $l_{5\sigma,1\pi} = 0{\cdot}217$, $B = 1{\cdot}32\ \text{cm}^{-1}$.

The spin splitting constant λ is determined by spin-spin coupling in the first order perturbation theory and by SOC in the second order[24]: $\lambda = \lambda_{ss} + \lambda_{so}$:

$$\lambda_{ss} = \tfrac{1}{2}D(^4\Sigma^-, \sigma\pi^2) = \tfrac{1}{6}(2D_{\sigma\pi} + D_{\pi\pi}) \qquad (14)$$

$$D_{\sigma\pi} = \sum_A (C^A_\pi)^2\, [(C^A_{\sigma,s})^2 - (C^A_{\sigma,z})^2]\, D^A_{sp} \qquad (15)$$

$D_{\pi\pi} = \sum_A (C^A_{2\pi})\, {}^4D_{p_xp_y}$; $D_{p_xp_y} = 2D_{sp} = 0{\cdot}032(z'_A)^3\ \text{cm}^{-1}$, where z'_A is the Slater charge of nucleus A. Using these equations we obtain $\lambda_{ss} = 0{\cdot}2002\ \text{cm}^{-1}$.

The SOC contribution to λ for the $a^4\Sigma^-$ state of CF is equal to:

$$2\lambda_{so} = \frac{|\langle X^2\Pi|\mathbf{H}_{SO}|\, a^4\Sigma^-\rangle|^2}{E(^4\Sigma^-) - E(X^2\Pi)} + \frac{|\langle b^4\Pi|\mathbf{H}_{SO}|\, a^4\Sigma^-\rangle|^2}{E(^4\Pi) - E(^4\Sigma^-)} +$$

$$+ \frac{\frac{1}{2}|\langle ^2\Sigma^+|\mathbf{H}_{SO}|\, a^4\Sigma^-\rangle|^2}{E(^2\Sigma^+) - E(^4\Sigma^-)} = \frac{\frac{1}{12}(B_{2\pi,5\sigma})^2}{24700} + \frac{\frac{1}{9}(B_{1\pi,5\sigma})^2}{53500} + \frac{\frac{1}{3}(B_{2\pi,2\pi})^2}{27000} = 0{\cdot}077\ \text{cm}^{-1}\,. \qquad (16)$$

The total spin splitting constant, λ, for the $a^4\Sigma^-$ state of CF amounts of $0{\cdot}2387\ \text{cm}^{-1}$.

Our predictions for the $a^4\Sigma^-$ state and for the $a^4\Pi - X^2\Pi$ transition of CF can be verified by observing the emission in a gase discharge and by its rotational analysis.

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* There are some discrepancies between our formulas (*12*) and (*16*) for the fine structure constants (λ, γ) and those, given in ref.[9]. It means that the second contribution in formula (*16*) is not equal to $A^2(^4\Pi)|\langle ^4\Sigma^-_{1/2}|L|^4\Pi_{1/2}\rangle|^2$ as used in ref. [9].

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