

SPECTROSCOPY OF NITROGEN: EFFICIENT ACCOUNT FOR POLARIZATION EFFECTS IN CALCULATIONS OF PROBABILITIES AND ENERGIES OF TRANSITIONS IN THE N₂ SPECTRUM

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Based on the modified method of motion equations taking into account the most important polarization effects, including the so-called two-particle-hole interactions the spectroscopic data on energies and strength of transition oscillators in the nitrogen molecule spectrum correcting earlier experimental and theoretical results have been obtained using the technique developed and tested in the previous papers.

The calculational results of spectroscopic characteristics are presented in this paper. They are the probabilities, strengths of oscillators, and energies of transitions in the nitrogen molecular spectrum which refine the theoretical and experimental data obtained earlier. The calculation was carried out based on the method of motion equations, the important polarization effects being effectively taken into account using the technique proposed and tested earlier. The presented data, some of which (oscillator strengths of the transitions $X^1\Sigma_g^+ \rightarrow b^1\Pi_u$ and $X^1\Sigma_g^+ \rightarrow b^1\Sigma_u^+$, etc.) have been obtained more or less accurately for the first time, can be used in some applications including atmospheric optics.

Introduction. As is well known, nitrogen is one of the basic components of the Earth's atmosphere. The N₂ molecular spectrum is of great interest, in particular, in studying the processes in the upper atmospheric layers in which the excited and ionized N₂ molecules (together with oxygen molecules) play an important role.^{1,2} Thus the first positive and first negative systems are observed in the spectra of the upper atmospheric air glow. The first and second positive systems of the N₂ bands and the first negative system of the N₂⁺ bands occur in the aurora spectra. Although the nitrogen molecule has been studied in a great number of papers,³⁻¹⁶ some spectroscopic parameters of this molecule have not been reliably established thus far, and some of them have been justified only theoretically and, unfortunately, they have not been experimentally verified. In particular, this is true with the oscillator strengths of transitions related to the bands of Geidone-Hermann ($X^1\Sigma_g^+ - b^1\Pi_u$), Bersger-Hopfield ($X^1\Sigma_g^+ \rightarrow b^1\Sigma_u^+$, etc.).

The most comprehensive study of the spectroscopic characteristics of the nitrogen molecule has evidently been done by Gilmore.^{5,6} The detailed review of the papers devoted to nitrogen spectroscopy is given in Ref. 12. A series of papers^{7-11,13,14} deals with calculations of potential curves, energy levels mainly of low-lying configurations of N₂ based on the methods of motion equations and the method of a model potential, as well as using the Hartree-Fock approximation that takes into account the configuration interaction. From the standpoint of taking into account the correlation that strongly contributes to energy characteristics of N₂, this molecule is related to the sufficiently complicated ones. As known, the correlation

effects are taken into account in the most accurate way either in a very complete approximation of configuration interaction, which is, as a rule, an extremely cumbersome and complicated problem, or within the framework of semiempirical models. In the latter case, however, one must be careful when interpreting the obtained data. In the recent paper¹⁴ the second positive system of nitrogen was calculated using a semiempirical method. The electron transition $a^1\Pi_g - X^1\Sigma_g^+$, as well as the lifetime of this state were, apparently, measured and calculated in the latest papers concerned with the N₂ molecule.^{13,14} In this paper the calculational results are given on the energy and strengths of oscillators of the electron transitions in the nitrogen molecule spectrum, which correct to a certain extent the theoretical and experimental spectroscopic data available. In particular, we have obtained new values of oscillator strengths for the electron transitions $X^1\Sigma \rightarrow b^1\Pi_u$, $X^1\Sigma_g^+ - b^1\Sigma_u^+$. The calculation was carried out using a modified method of motion equations, which differs from the standard method of motion equations developed by McKoy, et al.¹⁷⁻¹⁹ by the technique used for taking into account for the two-particle-hole polarization interactions. The effects related to these interactions can, e.g., contribute to energies of the electron transitions up to 3 eV and to ~30 % to the strengths of oscillators. As is well known, the theoretical determination of potential curves, energies, and probabilities of electron transitions in molecules requires that the preliminary calculations of wave functions and total energies of molecular states be made with a maximum attainable accuracy that naturally demands the adequate, and sometimes very substantial calculational efforts. In this respect, the method of motion equations seems to be a reliable alternative for the conventional quantum chemical methods.⁸⁻¹⁰ A specific feature of this method is the possibility of directly calculating the amplitudes of different processes, including photon absorption, etc., avoiding the problems associated with calculations of wave functions and total molecular energies. Naturally, the method does not provide for absolute accuracy as, e.g., the known limiting versions of variational solution of the problem do, nevertheless it is sufficiently effective for calculating frequencies and probabilities of transitions in molecules. As shown, in Refs. 17-19, to attain the acceptable accuracy of calculations it is possible to employ the bases of orbitals sufficiently limited in volume. However, in this case such important effects as "pressure of continuum," energy dependence of the self-consistent field potential, the effects

related to the so-called $2p - 2h$ (two particles – two holes) polarization interactions must be taken into account (see Refs. 18–23 and 24 and 25). The account for these effects based on the standard technique^{18,24} strongly complicates the calculations. In Refs. 20, 21 within the framework of the density functional formalism^{22,23} the effective procedure for taking into account the foregoing effects was developed by employing the energy-dependent exchange-polarization functionals. By way of example the spectra of the excited states, frequencies, and strengths of oscillators of the transition in molecules of benzol and formaldehyde were calculated to demonstrate the efficiency of the method. We shall give only a brief description of some principal stages of the calculations.

Method of calculation. According to Refs. 17 and 18, the operator Q_λ^+ generating the excited state $|\lambda\rangle$ of a molecule from the ground state $|O\rangle$, i.e., $|\lambda\rangle = Q_\lambda^+|O\rangle$, is the exact solution of the motion equation

$$\langle 0 | [\delta Q_\lambda, H, Q_\lambda^+] | 0 \rangle = \omega_\lambda \langle 0 | [\delta Q_\lambda, Q_\lambda^+] | 0 \rangle, \quad (1)$$

where ω_λ is the transition frequency and a double commutator is determined as

$$2[A, H, B] = [A, [H, B]] + [[A, H], B]. \quad (2)$$

Taking into account the excitations of the type of one particle – one hole $|1p - 1h|$ in Eq. (1), Eq. (1) can be reduced to a matrix equation for the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$:

$$\begin{bmatrix} A & B \\ -B^* - A^* & \end{bmatrix} \begin{bmatrix} Y(1) \\ Z(1) \end{bmatrix} = \omega_\lambda \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(1) \\ Z(1) \end{bmatrix}, \quad (3)$$

where the matrix elements A, B and D read

$$\begin{aligned} A_{m\gamma n\delta} &= \langle 0 | [C_{m\gamma}, H, C_{n\delta}^+] | 0 \rangle; \\ B_{m\gamma n\delta} &= \langle 0 | [C_{m\gamma}, H, C_{n\delta}] | 0 \rangle; \\ B_{m\gamma n\delta} &= \langle 0 | [C_{m\gamma}, C_{n\delta}^+] | 0 \rangle, \end{aligned} \quad (4)$$

and C^+ is a partially hole generator (C is the one of annihilation), the indices m and n stands here for particles states, γ and δ denote the hole states, H is the molecular Hamiltonian in the representation of the second quantization. To estimate the matrix elements⁴ the approximated wave function of the ground state is written in the form¹⁷

$$|0\rangle \approx N_0(1 + U) |HF\rangle, \quad (5)$$

$$\text{where } U = \frac{1}{2} \sum_{m\gamma n\delta} C_{m\gamma} C_{n\delta}^+, |HF\rangle$$

is the Hartree–Fock function.

Taking this definition into account the elements A, B and D take the forms

$$\begin{aligned} A_{m\gamma n\delta} &= A_{m\gamma n\delta}^0 + \delta_{\gamma\delta} \left[T_{mn} - \frac{1}{2} (\varepsilon_m + \varepsilon_n - 2\varepsilon_\gamma) \rho_{mn}^{(2)} \right] - \\ &- \delta_{mn} \left[T_{\gamma\delta} - \frac{1}{2} (2\varepsilon_m - \varepsilon_\gamma - \varepsilon_\delta) \rho_{\gamma\delta}^{(2)} \right]; \end{aligned}$$

$$B_{m\gamma n\delta} = B_{m\gamma n\delta}^{(0)} + (-1)^\lambda S_{m\gamma n\delta},$$

$$D_{m\gamma n\delta} = \delta_{mn} \delta_{\gamma\delta} + \delta_{mn} \rho_{\gamma\gamma}^{(2)} - \delta_{\gamma\delta} \rho_{mn}^{(2)}. \quad (6)$$

Here A^0 and B^0 are standard matrices of the random phase approximation¹⁸ and the other terms in Eq. (6) are

$$S_{m\gamma n\delta} = - \sum_{\rho\mu} \{ V_{m\mu n\delta} c_{\rho\mu n\gamma} + c_{\rho\mu m\delta} V_{n\mu\gamma\rho} \};$$

$$T_{\gamma\delta} = \frac{1}{2} \sum_{pq} \{ V_{pq\gamma\nu} c_{p\delta q\nu}^* + V_{\delta\nu p q} c_{p\gamma q\nu} \}; \quad (7)$$

$$T_{mn} = -\frac{1}{2} \sum_{q\mu\nu} \{ V_{mq\mu\nu} c_{n\mu q\nu}^* + V_{\mu\nu n q} c_{m\mu q\nu} \};$$

and then

$$V_{ijkl} = \langle i(1) j(2) | r_{12}^{-1} k(1) l(2) \rangle. \quad (8)$$

In Eqs. (6)–(8) the indices p and q as well as m and n are related to the particle states and μ and ν as well as γ and δ are related to the hole ones. The values ε_m and ε_γ , etc. in Eq. (6) determine the Hartree–Fock orbital energies, $\rho_{mn}^{(2)}$ and $\rho_{\gamma\delta}^{(2)}$ are the corrections to the second-order density matrix depending quadratically on correlation coefficients. If the correlation coefficients are neglected, the matrix elements of Eq. (6) are reduced to the corresponding matrix elements of the random-phase approximation.¹⁸ Using this approximation the motion equations for determining the $1p - 1h$ amplitudes $\{Y\}$ and $\{Z\}$ and the corresponding excitation energies are solved by the standard methods of matrix algebra. The approximation $1p - 1h$ in Eq. (1) being considered so far cannot, however, in most of the cases, provide sufficient accuracy in calculating spectroscopic characteristics of molecules.¹¹ Although the most important low-lying excited states are related to the $1p - 1h$ pairs and, in the complete expansion of Q_λ^+ , have the largest amplitudes, the components $2p - 2h$, i.e., those doubly excited with respect to the ground molecular state of configuration, are also important and can contribute to the energy of transition, e.g., to ~ 3 eV, (see Ref. 11). Their inclusion is relevant to the account for the self-consistent tuning of the hole orbitals during the virtual excitations in the frame of the basic molecular configuration. In this paper for the $2p - 2h$ effects to be taken into account we use the effective procedure developed in Ref. 20 which is based on the density functional formalism. The account of the $2p - 2h$ components in Q_λ^+ is equivalent to renormalization of matrices in Eq. (3) resulting in the ω dependence and, according to Refs. 22 and 23, is reduced to the appearance of the weight factor $a(\mathbf{r}) = [1 - \Sigma(\mathbf{r})]^{-1}$ in the matrix elements. In the density functional approximation the value $\Sigma(\mathbf{r})$ is defined as an electron density functional²⁰

$$\Sigma(\mathbf{r}) = -0.0834\rho^{1/3}(\mathbf{r}) - 0.0518\rho^{1/3}(\mathbf{r})/[1 + 18.377\rho^{1/3}(\mathbf{r})]. \quad (9)$$

It is difficult to calculate the matrix elements with the weighting factor $a(r)$. The calculation can be significantly simplified, without loss of accuracy, by replacing $a(\mathbf{r})$ by $a(0)$ according to the well-known and justified procedure in the theory of atomic photoeffect²⁵ which is based on approximation of random phases with exchange. It should

be noted now that the foregoing amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ determine the moment of transition $M_{0\lambda}$

$$M_{0\lambda} = \sqrt{2} \sum_{m\gamma} \{Y_{m\gamma}^*(\lambda) M_{m\lambda} + Z_{m\gamma}^*(\lambda) M_{m\lambda}\}. \quad (10)$$

The oscillator strength of the transition $|0\rangle - |\lambda\rangle$ is determined in terms of $M_{0\lambda}$ as follows:

$$f_{0\lambda} = \frac{2}{3} G \omega_\lambda M_{0\lambda}^2, \quad (11)$$

where G is the degeneration factor. The calculational scheme employed in this paper fully corresponds to that of the conventional motion-equations method, except for consideration of the $2p - 2h$ effects. Let us now represent calculational results on energies and oscillator strengths of the electron transitions in the nitrogen molecule.

Calculational results. The electron configuration of the nitrogen molecule in the ground state is $(1\sigma_g)^2 (1\sigma_u)^2 (2\sigma_g)^2 (2\sigma_u)^2 (\pi_{uy})^2 (\pi_{yx})^2 (3\sigma_g)^2$. The geometry chosen for calculations is taken in accordance with the conventional experimental geometry of this molecule in the ground state.¹² The first step is to conduct the Hartree-Fock calculation for generating the particle-hole basis. A self-consistent calculation is carried out in the basis of Gaussian orbitals. We use the basis [4 s + 3 p] of contracted Gaussian orbitals completed with diffusion functions (the detailed description of the basis can be found, e.g., in Ref. 11). The particle and hole energy levels are given in Table I. Here the molecular orbitals 8–13 are the diffusion ones.

TABLE I. Self-consistent molecular orbital energies in N₂ (eV).

No.	MO	ϵ_γ	No.	MO	ϵ_m
1	$1\sigma_g$	-15.7079	17	$5\sigma_u$	0.5869
2	$1\sigma_u$	-15.7043	18	$3\pi_{gx}$	0.6114
3	$2\sigma_g$	-1.5255	19	$3\pi_{gy}$	0.6514
4	$2\sigma_u$	-0.7727	20	$5\sigma_g$	0.8602
5	π_{ux}	-0.6240	21	$6\sigma_u$	1.0232
6	π_{uy}	-0.6240	22	$7\sigma_u$	1.5413
7	$3\sigma_g$	-0.6271	23	$4\pi_{gx}$	1.6651
8	$3\sigma_u$	0.0257	24	$4\pi_{gy}$	3.6651
9	$1\pi_{gx}$	0.0910	25	$3\sigma_{ux}$	3.0148
10	$1\pi_{gy}$	0.0910	26	$3\pi_{uy}$	3.0148
11	$4\sigma_u$	0.1632	27	$8\sigma_u$	3.0819
12	$2\pi_{gx}$	0.1654	28	$6\sigma_g$	3.3528
13	$2\pi_{gy}$	0.1654	29	$5\pi_{gx}$	3.9962
14	$2\pi_{ux}$	0.5320	30	$5\pi_{gy}$	3.9962
15	$2\pi_{uy}$	0.5320	31	$9\sigma_u$	33.2482
16	$4\sigma_g$	0.5460	32	$7\sigma_g$	33.5275

Table II lists the values of energies of the excited states of the nitrogen molecule calculated in this paper and the results calculated using the method of motion equations in the $1p - 1h$ approximation and in the $2p - 2h$ approximation based on the technique taken from Ref. 11. The experimental data^{6,12} are also given in this table.

TABLE II. Energies of excited states of the N₂ molecule (eV).

State	$\Delta E(1p - 1h)$ Ref. 11	$\Delta E(1p - 1h + 2p - 2h)$ Ref. 11	$\Delta E(2p - 2h)$ Our results	ΔE experiment Ref. 12
$B^3\Pi_g$	9.6	7.5	8.06	8.1
$a^4\Pi_g$	11.5	8.8	9.66	9.3
$A^3\Sigma_u^+$	8.4	7.8	7.14	7.8
$B'^3\Sigma_u^-$	11.3	10.2	9.50	9.7
$W^3\Delta_u$	10.1	9.4	8.59	8.9
$a^1\Sigma_u^-$	11.3	10.6	9.61	9.9
$\omega^1\Delta_u$	12.0	11.0	10.20	10.3
$b^1\Sigma_u^+$	16.8	15.0	14.28	14.4
$c^1\Sigma_u^+$	15.5	12.1	13.17	12.9
$C^3\Pi_u$	13.3	10.8	11.30	11.1
$b^1\Pi_u$	17.4	14.0	13.92	12.8

It can be seen from the table that an account of $2p - 2h$ interactions is needed in principle. The error in calculations within the framework of the $1p - 1h$ approximation, as can be seen from the comparison of the experimental and calculational values of transitions, attains ~20 %. The transition energies obtained in this paper are in a good agreement with those obtained experimentally. With the exception for the transition $A^3\Sigma_u^+$ the error of calculating the sought-after energies, in comparison with experimental results, does not exceed several percent.

As can be seen from the analysis, for the transition to $A^3\Sigma_u^+$ the correction of the transition energy for $2p - 2h$ polarization effects turns out to be the smallest as compared to the remaining transitions. Consequently, the contribution of the $2p - 2h$ effect to this transition turns out to be overestimated. The largest correction of the transition energy for these effects is observed for the transitions to the states $b^1\Pi_u$ and $c^1\Sigma_u^+$, $a^4\Pi_g$. It is obvious that the technique for taking into account the $2p - 2h$ effects used in calculations for these transitions underestimates somewhat the sought-after effects.

TABLE III. Oscillator strengths of the N₂ molecule transition (see the text).

Transition	Ref. 11	Our results	Experiment
$X^1\Sigma_g^+ - c^1\Sigma_u^+$	0.11	0.10	0.14 ± 0.04
$X^1\Sigma_g^+ - b^1\Pi_u$	0.32	0.26	< 0.3
$X^1\Sigma_g^+ - b^1\Sigma_u^+$	0.49	0.39	0.83
			0.40

The $2p - 2h$ polarization interactions have been taken into account in the most effective way for the transitions to the states $B^3\Pi_g$, $B'^3\Sigma_u^-$, $\omega^1\Delta_u$, $b^1\Sigma_u^+$ and $C^3\Pi_u$ and the obtained energies of the transitions to these states are in a good agreement with recommended experimental values. Table III lists the calculational results on the oscillator strengths for some transitions in the N₂ molecule spectrum as well as the available theoretical estimates and experimental recommendations. The most comprehensive

information is available for the transition $X^1\Sigma_g^+ - c'^1\Sigma_u^+$. The value of the oscillator strengths given in Ref. 11 for this transition are somewhat lower than those recommended from the experiment. The value f obtained in this paper is equal to 0.10 and is also somewhat lower than the experimental ones. It should be noted that the spread of the experimental value is about 30 % for the transition $X^1\Sigma_g^+ - c'^1\Sigma_u^+$. The other transitions under consideration, in particular, $X^1\Sigma_g^+ \rightarrow b^1\Pi_u$ and $X^1\Sigma_g^+ \rightarrow b'^1\Sigma_u^+$, are sufficiently complicated. The matter is that, e.g., for the transition to $b^1\Pi_u$ it is difficult to estimate the Franck-Condon factor. There occurs a strong disturbance of the levels of the $b^1\Pi_u$ state by the $c^1\Pi_u$ state. There is no experimental value of the oscillator strength for this transition, only the estimate $f < 0.3$ is available. The value of f obtained in this paper is equal to 0.26. However, for the transition $X^1\Sigma_g^+ - b'^1\Sigma_u$ the values of the oscillator strengths do not agree. Rose et al.¹¹ obtained the value 0.49 for the oscillator strength of this transition without taking the value of the Franck-Condon factor into account. The value of f recommended in this paper is 0.39.

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