

X-ray absorption spectra of the nitromethane molecule CH_3NO_2

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(Received 25 December 1991)

Opt. Spektrosk. 72, 1094–1101 (May 1992)

The transmission method using characteristic x-ray lines was used to measure the spectral dependence of the absorption cross section of the nitromethane molecule CH_3NO_2 over a wide range of quantum energies, 270–780 eV. In the region of the K absorption edges of carbon, nitrogen and oxygen atoms, the cross-section measurements were made with high energy resolution, $\Delta E = 0.2$ – 0.7 eV, using continuous bremsstrahlung. The near fine structure of the NK and OK absorption spectra of the nitromethane molecule was interpreted on the basis of a comparative analysis of the spectra in CH_3NO_2 with NO_2 : the fundamental absorption bands A , B , and C – C' are associated with transitions of the inner electrons to free molecular states (form resonances), which are described by the antibonding MOs of the CNO_2 fragment $b_1\pi$ (N – O), $a_1\sigma$ (N – C), and $a_1, b_2\sigma$ (N – O). These MOs have significant contributions from atomic $2p$ states. The determining role (from the standpoint of the strength of the absorption bands) of atomic $2p$ states is confirmed by a quantitative comparison of the experimentally obtained oscillator strengths for transitions to π and σ states. On the basis of an analysis of the total oscillator strengths of the x-ray transitions to molecular states having contributions of the $2p$ states of the nitrogen atoms for the N_2 and CH_3NO_2 molecules, the $2p$ partial effective charge of the nitrogen atom in CH_3NO_2 was estimated (0.6 for N_2 in the presence of O).

Previous studies of the x-ray absorption spectra (XAS) of a series of simple molecular compounds of atoms of the second period of the periodic table^{1–20} demonstrated a high information content of the near fine structure (NFS) of these spectra in terms of the study of the electronic and atomic structure of these molecules. This is largely due to the fact that the molecular form resonances that are dominant in the NFS result from the trapping, during photoabsorption, of K electrons in free molecular orbitals (MOs), built up mainly of atomic $2p$ states.^{6,7,9,10} In the case of linear or planar molecules, the sharp anisotropy of the molecular potential causes a marked energy splitting of the atomic $1s$ – $2p$ resonance into σ and π components (molecular form resonances), oriented along the bond line ($\sigma 2p$) and at right angles to it ($\pi 2p$).^{6,9,10} The energy splitting of the atomic resonance, $\Delta E(\pi - \sigma)$, which characterizes the anisotropy of the molecular potential, is largely determined by the interatomic distance,^{6,9,13–15} and hence can be used to determine the latter experimentally. In turn, the absolute energy positions and intensities (oscillator strengths) of the resonance absorption bands are related to the chemical state (effective charges) of the atoms in the molecular compounds.^{9–12,15,16,19} The main purpose of this paper is to extend the methods of analyzing the resonance characteristics that were developed for the spectra of simple molecules to the more complex molecule of nitromethane CH_3NO_2 ,¹⁹ whose carbon, nitrogen and oxygen atoms are known to be coplanar.^{21,22}

The spectral dependences of the photoabsorption cross sections σ of the nitromethane molecule were studied by transmission with the aid of an RSM-500 x-ray monochromator–spectrometer.²³ The absorption cross sections were measured over a wide range of quantum energies (270–780 eV) at the characteristic x-ray lines, while,

in the region of the ionization K thresholds of carbon, nitrogen, and oxygen atoms, the bremsstrahlung cross sections were measured with energy resolution $\Delta E \approx 0.2$ eV (CK spectrum), $\Delta E \approx 0.4$ eV (NK spectrum), and $\Delta E \approx 0.7$ eV (OK spectrum). The energies of the NFS elements of the resulting XAS were referenced to the characteristic x-ray lines: $\text{Cr}L_\alpha$ (21.64 Å; second order), $\text{Fe}L_I$ (20.15 Å; second order), $\text{Ti}L_I$ (31.36 Å), $\text{Ti}L_\alpha$ (27.42 Å); $\text{Cr}L_\alpha$ (21.64 Å)²⁴ and OK_α in MgO (23.599 Å).²⁵ The gas pressure in the cell was measured with a VDG-1 gas-discharge deformation vacuum gauge, previously calibrated with a mercury and oil manometer to within 5%. The total error in determining σ at the characteristic x-ray lines was 10%, and, for the bremsstrahlung, 20%. The remaining details of the method for obtaining the spectra are described in previous papers.^{1–5,10,12}

Figure 1 shows the spectral dependence, obtained for this paper, of the photoabsorption cross section σ of the CH_3NO_2 molecule in the quantum energy range $\hbar\omega = 270$ – 780 eV; arrows indicate the positions of the CK (293.04 eV), NK (411.16 eV), and OK (539.12 eV) absorption edges of the nitromethane molecule.²⁶ The measured results of the cross sections for photoabsorption at the characteristic x-ray lines (Table I), shown by circles in Fig. 1, are quite consistent with measurements using continuous bremsstrahlung (solid lines). It should also be noted that the experimentally measured photoabsorption cross sections of the CH_3NO_2 molecule far from the absorption edges are in good agreement with the cross sections calculated as the sum of the atomic photoabsorption cross sections²⁷ (Table I).

An examination of the NFS of the absorption spectra of the nitromethane molecule (Fig. 2, Table II) clearly shows that, in the NK and OK spectra, two intense A and

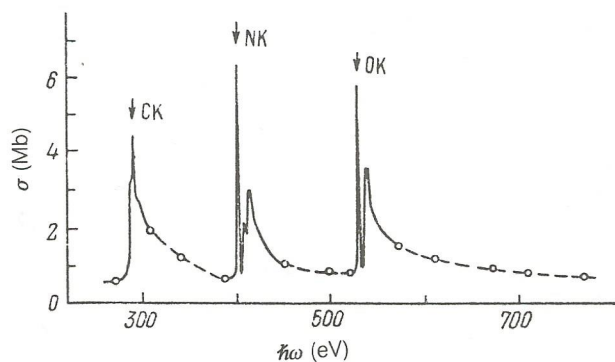


FIG. 1. Spectral dependence of the photoabsorption cross section of the nitromethane molecule CH_3NO_2 in the range of quantum energies $\hbar\omega = 270\text{--}780$ eV. Circles denote absorption cross sections measured from the characteristic x-ray lines; the solid curve shows the values measured from bremsstrahlung; the dashed line shows interpolated σ values. Arrows indicate the positions of the CK, NK, and OK ionization thresholds in CH_3NO_2 from the data of Ref. 26.

C bands dominate, the latter being located above the ionization threshold, i.e., in the continuum. Significantly, the energy absorptions of these bands relative to the ionization thresholds practically coincide in the two spectra. In turn, the NFS of the CK spectrum is characterized by narrower and less intense peaks (relative to the continuous absorption level), located only before the ionization threshold in its immediate vicinity and having no obvious analogues in the NFS of the nitrogen and oxygen spectra. In addition, in general form and in the energy positions of the structural details relative to the ionization threshold, this spectrum of the CH_3NO_2 molecule correlates well with the CK spectra of the methyl groups CH_3 in other CH_3X molecules, where $\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OH},$ or NH_3 ,^{5,28–32} $(\text{CH}_3)_4\text{Si}$,³³ $(\text{CH}_3)_3\text{P}$,³⁴ and $(\text{CH}_3)_2\text{SO}$.³⁵

Based on these experimental facts, it is natural to regard the CH_3NO_2 molecule as a combination of two simpler atomic groups (quasimolecules, or fragments), i.e., the ions CH_3^+ and NO_2^- , whose interaction does not ap-

TABLE I. Photoabsorption cross sections (Mb) for the nitromethane molecule CH_3NO_2 , measured from the characteristic x-ray lines (σ) and calculated as the sum of the atomic absorption cross sections ($\sum \sigma_i$) (Ref. 27).

Line	Quantum energy $\hbar\omega$ (eV) (Ref. 24)	σ (Mb)	$\sum \sigma_i$, Mb
CK_α	277.4	0.41	0.308
CaL_I	302.7	1.93	—
CaL_α	341.3	1.14	—
TiL_I	395.2	0.64	0.672
TiL_α	452.4	0.98	1.029
CrL_I	500.3	0.83	—
OK_α	525.5	0.74	0.713
CrL_α	572.9	1.54	1.516
FeL_I	615.3	1.32	—
CoL_I	677.8	1.04	—
FeL_α	704.8	0.83	0.987
CoL_α	776.2	0.75	0.712

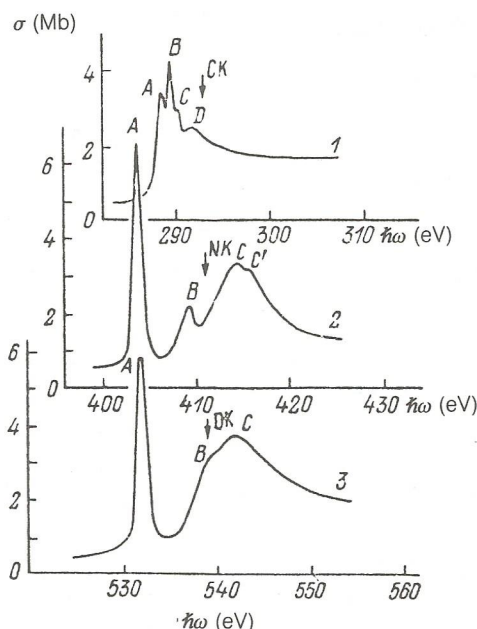


FIG. 2. Near fine structure of the K absorption spectra of atoms of carbon (1), nitrogen (2), and oxygen (3) in the nitromethane molecule CH_3NO_2 . The spectra coincide in energy with the positions of the corresponding ionization thresholds.²⁶

preciably alter the spectral distribution of the oscillator strengths of the x-ray transitions in the atoms belonging to each of the groups. This approach is also supported by our study of the K absorption spectrum of the nitroethane molecule $\text{C}_2\text{H}_5\text{NO}_2$ (Fig. 3). The structure of this spectrum differs little from the NFS of the corresponding spectrum of the CH_3NO_2 molecule: the replacement of methyl groups CH_3 by ethyl groups C_2H_5 is associated with only a small decrease of the strength of the A and B absorption bands. Thus, the structure of the nitrogen and oxygen spectra in the CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ molecules is chiefly determined by the system of excited states of the NO_2^- anion.

Let us compare the resulting NK absorption spectra of the nitromethane and nitroethane molecules with the K spectrum of the nitrogen in the free NO_2 molecule³⁶ (Fig. 3). Despite the correlation of the principal details of the structure (the A and C bands), there are appreciable differences: the presence in the NO_2 spectrum of an additional intense band A' and of low-intensity narrow peaks a–c before the NK ionization threshold, as well as the absence of any obvious analogue of the B band from the spectrum of nitrogen dioxide. A similar situation is found when the OK absorption spectra of CH_3NO_2 and NO_2 are compared (Fig. 4).

The NO_2 molecule in the ground state has C_{2v} symmetry. The ground state is described by means of single-electron MOs as follows:^{36–38} $1b_2^2$ ($\text{O}1s$) $1a_1^2$ ($\text{O}1s$) $2a_1^2$ ($\text{N}1s$) $3a_1^2$ $2b_2^2$ $4a_1^2$ $5a_1^2$ $3b_2^2$ $1b_1^2$ $1a_2^2$ $4b_2^2$ $6a_1^1$, $^2A_1$. The first absorption band A' in the NO_2 spectra is attributed to dipole-allowed transitions of NK and OK electrons to the half-filled MO $6a_1$, and the A and C bands are attributed to transitions to the lower free $2b_1$ MO (antibonding, π type)

TABLE II. Energy positions E (eV) and oscillator strengths f of the absorption hands in the K spectra of the CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ molecules.

Absorption bands	CH_3NO_2					$\text{C}_2\text{H}_5\text{NO}_2$	
	OK spectrum		NK spectrum		CK spectrum	NK spectrum	
	E	$f \cdot 10^2$	E	$f \cdot 10^2$	E	E	$f \cdot 10^2$
A	531.7	5.6 ± 0.8	403.9	6.8 ± 0.9	288.7	403.7	6.5 ± 0.9
B	—	—	409.15	2.0 ± 0.4	289.6	409.3	1.4 ± 0.3
C	542.2	13 ± 3	414.45	10 ± 2	290.4	413.6	11 ± 2
C'	—	—	415.9	2.1 ± 0.4	—	415.0	3.0 ± 0.5
D	—	—	—	—	291.5	—	—

and to the energetically higher antibonding σ MO $5b_2$.³⁶ According to calculations made in the work cited, in the spectrum of free molecular states of the NO_2 molecule, there is one more state, described by the antibonding $7a_1$ MO, which, like the semifree bonding $6a_1$ MO, is oriented in the plane of the molecule along the twofold symmetry axis C_2 . Transitions of the inner electrons to this state are associated with the production in the spectra of NO_2 of the weak band B , energetically located in the region of the a -c Rydberg states of the molecule. In view of the above, it is natural to attribute the absence of the A' band from the spectra of the CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ molecules to the fact that the NO_2 group in the nitromethane and nitroethane molecules attracts an additional electron from the methyl or ethyl group; this leads to occupation of the $6a_1$ MO, and hence, to the impossibility of transitions of K electrons to this MO in CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$. That the NO_2 group in these molecules carries a negative charge is indicated by the simultaneous shift of the binding energies of the NK and OK electrons in the CH_3NO_2 molecule toward lower values (411.16, 539.12 eV) in comparison with the neutral NO_2 molecule (412.6, 541.3 eV).²⁶ The presence of an excess electron on the NO_2 group in the CH_3NO_2 molecule

gives rise to a positive charge of almost unity on the methyl group, and this in turn is in good agreement with the experimental fact that the K ionization thresholds of the carbon atom are similar in the CH_3NO_2 (293.04 eV) and CH_3F (293.6 eV) molecules.²⁶

In the quasimolecular NO_2 approach used here, the first absorption band A in the CH_3NO_2 spectra should be attributed to transitions of the K electrons of the nitrogen and oxygen atoms to a free molecular state of πb_1 symmetry. Indeed, adding the carbon atom of the methyl group to the NO_2 molecule along the direction of the C_2 symmetry axis (in the molecular plane) will not result in any appreciable change of the πb_1 state, which is oriented perpendicular to the molecular plane in the NO_2 molecule. This qualitative consideration is consistent with the experimental fact that the energy of the N (O) $K \rightarrow \pi b_1$ transitions changes only slightly in the series $\text{NO}_2 \rightarrow \text{CH}_3\text{NO}_2 \rightarrow \text{C}_2\text{H}_5\text{NO}_2$. Since the molecular potential of CH_3NO_2 is chiefly determined by the CNO_2 fragment, which, like the NO_2 molecule, has C_{2v} symmetry, the symmetry of the states in this approximation is preserved when going from NO_2 to CH_3NO_2 .

At the same time, the presence of the CH_3 group in the nitromethane molecule, having no major effect on the πb_1 state, causes appreciable changes in the system of σ MOs oriented in the molecular plane of the CNO_2 fragment. In the NO_2 molecule, the two σ bonds between the nitrogen

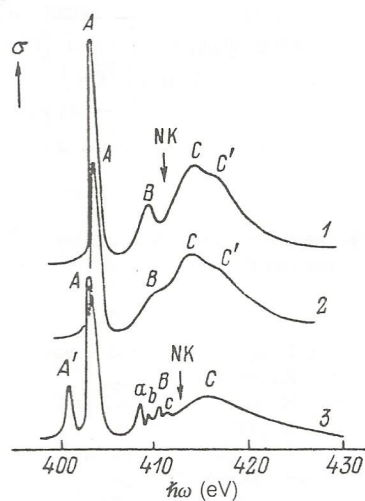


FIG. 3. NK absorption spectra of the CH_3NO_2 , $\text{C}_2\text{H}_5\text{NO}_2$, and NO_2 molecules.³⁶ The arrows indicate the positions of the NK ionization thresholds in the CH_3NO_2 and NO_2 molecules.²⁶

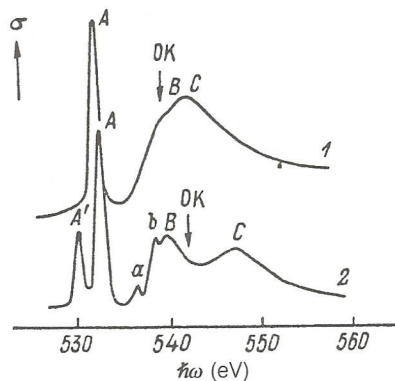


FIG. 4. OK absorption spectra of the CH_3NO_2 and NO_2 molecules.³⁶ The arrows indicate the positions of the OK ionization thresholds in the CH_3NO_2 and NO_2 molecules.²⁶

and oxygen atoms are formed by two bonding MOs of a_1 and b_2 symmetry. As a consequence, the absorption spectra of NO_2 exhibit two bands, B and C , associated with electronic transitions to free molecular states, which are described by the antibonding partners of these bonding MOs. In the case of CH_3NO_2 , one more σ bond is added, between the nitrogen and carbon atoms and is oriented along the C_2 symmetry axis. This in turn leads to the inclusion in the σ bonding of one more MO of a_1 symmetry, and hence, to the possibility that the CH_3NO_2 spectra will have one more dipole-allowed transition, to the antibonding state of a_1 symmetry. From the appearance of the NO_2 and CH_3NO_2 spectra (Figs. 3 and 4), it is natural to assume that the B band in the CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ spectra is due to this transition, while the C and C' bands are due to transitions to the states that describe the σ bonds between the nitrogen and oxygen atoms.

In general, the above examination of the σ states of CH_3NO_2 represents going beyond the scope of the quasimolecular NO_2 approximation, since it considers the interaction of the NO_2 molecule with the carbon atom of the methyl group, i.e., the CNO_2 fragment is considered. Thus, on the basis of the expanded quasimolecular (fragmentary) approach, one can completely identify the structure of the NK and OK absorption spectra of the CH_3NO_2 molecule, attributing the A , B , C , and C' bands to dipole-allowed electronic transitions to the free antibonding MOs $b_1\pi(\text{N-O})$, $a_1\sigma(\text{N-C})$, $b_1\sigma(\text{N-O})$, and $a_1\sigma(\text{N-O})$. The high intensity of these transitions, as in the spectra of other compounds of the atoms of the second period of the periodic table, is determined by the sizable contributions to the final MOs of the atomic $2p$ states, which are strongly localized in the molecular region.

As noted above, the CK absorption spectrum of the nitromethane molecule CH_3NO_2 resembles in structure the CK spectra of the methyl group CH_3 in other molecules. Using the results of Refs. 5, 28–35, and 39, the A – C bands in the carbon spectrum can be attributed to transitions to excited states similar in nature to the Rydberg $3s$, $3p$, and $4p$ states of the united atom. At the same time, the values obtained for the absorption cross sections in the region of the CK edge (Figs. 1 and 2) give ~ 0.12 for the total oscillator strength of the discrete CK absorption in CH_3NO_2 , which is substantially higher than the oscillator strength (~ 0.01) of the discrete Rydberg transitions in the Ne atom and the N_2 molecule.¹² On this basis, it can be stated¹² that the excited states manifested in the CK spectrum of nitromethane contain appreciable contributions of atomic $2p$ states, and hence are similar in properties to molecular resonances. As for the D band in the CK spectrum, its correlation in energy position with the B band in the NK spectrum makes it possible to postulate that it has a similar origin, i.e., that it is associated with the antibonding MO $a_1\sigma(\text{C-N})$.

As is well known,^{6,9,13–15} the energy splitting $\Delta E(\pi - \sigma)$ of the components of atomic $2p$ states is directly related to the interatomic distance, and, in this case, to the distance $d(\text{N-O})$ between the nitrogen and oxygen atoms. It is clear (Fig. 3) that the transition from the free NO_2

molecule to the NO_2^- anion in the CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ molecules is accompanied by an appreciable decrease of the energy spacing $\Delta E(\pi - \sigma)$ between the π and σ form resonances (bands A and C – C'). Indeed, in the NK spectrum of CH_3NO_2 , $\Delta E(\pi - \sigma) = (10.6 + 12.0)/2 = 11.3$ eV (Table II), whereas, in the spectrum of the NO_2 molecule, it is 12.9 eV.³⁶ Such a change in $\Delta E(\pi - \sigma)$ indicates an appreciable increase of the interatomic distance d (N-O) in going from the NO_2 molecule to the CH_3NO_2 molecule, as is actually the case: for NO_2 , $d(\text{N-O}) = 1.193$ Å,³⁷ and, for CH_3NO_2 , $d(\text{N-O}) = 1.23$ Å.^{21,22}

Finally, we analyze the results for the absolute absorption cross sections σ for the CH_3NO_2 molecule in the region of the NK and OK absorption edges. The oscillator strengths for the transitions of K electrons to excited molecular states (the form resonances), obtained by graphically integrating the experimental dependences $\sigma(\hbar\omega)$,¹⁾ are listed in Table II. The ratio of oscillator strengths of the $1s \rightarrow \pi 2p$ and $1s \rightarrow \sigma 2p$ transitions (the A and B – C – C' bands) is 1:2 within experimental error. This is in agreement with the ratio of the statistical weights of the free atomic $2p_x$ and $2p_{y,z}$ states, which play a determining role in the approach employed here in forming the π and σ form resonances in the spectra of planar molecules.

In turn, the total sum of the oscillator strengths of transitions to the π and σ states, f_K^{2p} , is determined by the number of free $2p$ states of the atom in the chemical compound, and hence characterizes the occupancy by electrons of the $2p$ shell of the atom when the latter enters into a chemical bond. Thus, the changes observed in the total oscillator strength f_K^{2p} in going from one chemical compound to another can be used in quantitatively characterizing the $2p$ charge state (determining the $2p$ partial effective charge) of the absorbing atom.¹²

In the nitrogen atom, the $2p$ orbital contains three electrons, and the total oscillator strength f_K^{2p} in the N_2 molecule in terms of one nitrogen atom is 0.15.¹⁰ For the nitromethane and nitroethane molecules, $f_K^{2p} \approx 0.18$. Using this value, and assuming that f_K^{2p} is proportional to the number of free $2p$ states of the nitrogen atom, we find for the $2p$ partial effective charge of the nitrogen atom in CH_3NO_2 and $\text{C}_2\text{H}_5\text{NO}_2$ the value $q_N(2p) \approx +0.6$ [the value of $q_N(2p)$ in the N_2 molecule is taken as zero]. We note for comparison that the value $q_N(2p) = -1.8$ was previously obtained in a similar way for the ammonia molecule.¹²

¹⁾The σ resonance in the CH_3NO_2 spectra was distinguished from the background of the continuous spectrum by the method used previously for the NO_2 spectrum.¹²

¹A. S. Vinogradov, B. Shlarbaum, and T. M. Zimkina, *Opt. Spektrosk.* **36**, 658 (1974) [*Opt. Spectrosc. (USSR)* **36**, 383 (1974)].

²A. S. Vinogradov, T. M. Zimkina, V. N. Akimov, and B. Shlarbaum, *Izv. Akad. Nauk SSSR Ser. Fiz.* **38**, 508 (1974).

³V. I. Akimov, A. S. Vinogradov, and T. M. Zimkina, *Opt. Spektrosk.* **53**, 109 (1982) [*Opt. Spectrosc. (USSR)* **53**, 63 (1982)].

⁴V. N. Sivkov, V. N. Akimov, A. S. Vinogradov, and T. M. Zimkina, *Vestn. Leningradsk. Gos. Univ. Ser. Fiz. Khim.* No. 10, 79 (1983).

⁵V. N. Sivkov, V. N. Akimov, A. S. Vinogradov, and T. M. Zimkina, *Opt. Spektrosk.* **57**, 265 (1984) [*Opt. Spectrosc. (USSR)* **57**, 160 (1984)].

- ⁶V. N. Akimov, A. S. Vinogradov, A. A. Pavlychev, and V. N. Sivkov, *Opt. Spektrosk.* **59**, 342 (1985) [*Opt. Spectrosc. (USSR)* **59**, 206 (1985)].
- ⁷A. S. Vinogradov, V. N. Akimov, T. M. Zimkina, and A. A. Pavlychev, *Izv. Akad. Nauk SSSR Ser. Fiz.* **49**, 1458 (1985).
- ⁸V. N. Sivkov, V. N. Akimov, A. S. Vinogradov, and T. M. Zimkina, *Opt. Spektrosk.* **60**, 318 (1986) [*Opt. Spectrosc. (USSR)* **60**, 194 (1986)].
- ⁹A. A. Pavlychev and A. S. Vinogradov, *Opt. Spektrosk.* **62**, 329 (1987) [*Opt. Spectrosc. (USSR)* **62**, 197 (1987)].
- ¹⁰A. V. Zhadenov, V. N. Akimov, and A. S. Vinogradov, *Opt. Spektrosk.* **62**, 340 (1987) [*Opt. Spectrosc. (USSR)* **62**, 204 (1987)].
- ¹¹V. N. Sivkov, V. N. Akimov, and A. S. Vinogradov, *Opt. Spektrosk.* **63**, 275 (1987) [*Opt. Spectrosc. (USSR)* **63**, 162 (1987)].
- ¹²V. N. Akimov, A. S. Vinogradov, and A. V. Zhadenov, *Opt. Spektrosk.* **65**, 349 (1988) [*Opt. Spectrosc. (USSR)* **65**, 210 (1988)].
- ¹³S. V. Nekipelov, V. N. Akimov, and A. S. Vinogradov, *Fiz. Tverd. Tela (Leningrad)* **30**, 3647 (1988) [*Sov. Phys. Solid State* **30**, 2095 (1988)].
- ¹⁴S. V. Nekipelov, V. N. Akimov, and A. S. Vinogradov, *Opt. Spektrosk.* **64**, 817 (1988) [*Opt. Spectrosc. (USSR)* **64**, 487 (1988)].
- ¹⁵A. A. Pavlychev and A. S. Vinogradov, *Problems of Solid State Electronics*, No. 11. *Molecular and Electronic Processes at Phase Boundaries* (Leningrad, 1989), pp. 132–150.
- ¹⁶A. A. Pavlychev, A. S. Vinogradov, V. N. Akimov, and S. V. Nekipelov, *Phys. Scripta* **41**, 160 (1990).
- ¹⁷S. V. Nekipelov, V. N. Akimov, and A. S. Vinogradov, *Fiz. Tverd. Tela (Leningrad)* **33**, 663 (1991) [*Sov. Phys. Solid State* **33**, 378 (1991)].
- ¹⁸A. A. Pavlychev and A. S. Vinogradov, in *Proceedings of the UK/USSR Seminar "Today and Tomorrow in Photoionization," Leningrad 23–27 April 1990*, edited by M. Ya. Amusia and J. B. West (DL/SCI/R29), pp. 124–128.
- ¹⁹V. N. Akimov, A. S. Vinogradov, A. V. Zhadenov, and S. V. Nekipelov, in *Abstracts of the Fifteenth International Conference on X-Ray and Inner Processes*, (Knoxville, Tennessee, 1990), p. CO 8.
- ²⁰A. S. Vinogradov, S. V. Nekipelov, and A. A. Pavlychev, *Fiz. Tverd. Tela (Leningrad)* **33**, 896 (1991) [*Sov. Phys. Solid State* **33**, 508 (1991)].
- ²¹L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, *Determination of the Geometric Structure of Free Molecules* (Leningrad, 1978).
- ²²A. P. Cox, *J. Mol. Struct.* **97**, 61 (1983).
- ²³A. P. Lukirskii, N. A. Brytov, and N. P. Komyak, *Equipment and Methods for X-Ray Diffraction Analysis* (Leningrad, 1967), No. 2, pp. 4–19.
- ²⁴J. A. Bearden, *Rev. Mod. Phys.* **39**, 78 (1967).
- ²⁵H. -U. Chun and D. Hendel, *Z. Naturforsch.* **22a**, 1401 (1967).
- ²⁶A. A. Bakke, H. -W. Chen, W. L. J. Jolly, *Electron Spectr. Rel. Phenom.* **20**, 333 (1980).
- ²⁷B. L. Henke, P. Lee, T. J. Tanaka *et al.*, *Atom. Data Nucl. Data Tables* **27**, 1 (1982).
- ²⁸F. C. Brown, R. Z. Bachrach, and A. Bianconi, *Chem. Phys. Lett.* **54**, 425 (1978).
- ²⁹A. P. Hitchcock and C. E. Brion, *J. Electron. Spectr. Rel. Phenom.* **17**, 139 (1979).
- ³⁰G. E. Wight and C. E. Brion, *J. Electron. Spectr. Rel. Phenom.* **4**, 25 (1974).
- ³¹I. Ishii and A. P. Hitchcock, *J. Electron. Spectr. Rel. Phenom.* **46**, 55 (1988).
- ³²A. P. Hitchcock and C. E. Brion, *J. Electron. Spectr. Rel. Phenom.* **13**, 193 (1978).
- ³³R. N. S. Sodhi, S. Daniel, and C. E. Brion, *J. Electron. Spectr. Rel. Phenom.* **35**, 45 (1985).
- ³⁴R. N. S. Sodhi and C. E. Brion, *J. Electron. Spectr. Rel. Phenom.* **37**, 97 (1985).
- ³⁵K. H. Sze, C. E. Brion, M. Tronc, S. Bodeur, and A. P. Hitchcock, *Chem. Phys.* **121**, 274 (1988).
- ³⁶W. Zhang, K. H. Sze, C. E. Brion, X. M. Tong, and J. M. Li, *Chem. Phys.* **140**, 265 (1990).
- ³⁷G. Herzberg, *Electronic Spectra and the Structure of Polyatomic Molecules* (Van Nostrand, Princeton, N.J., 1968; Moscow, 1969).
- ³⁸V. N. Nefedov and V. I. Vovna, *Electronic Structure of Chemical Compounds* (Moscow, 1987).
- ³⁹V. N. Akimov, A. S. Vinogradov, and T. M. Zimkina, *Opt. Spektrosk.* **53**, 476 (1982) [*Opt. Spectrosc. (USSR)* **53**, 280 (1982)].