CHANGES IN THE UV ABSORPTION SPECTRA OF NITRIC OXIDE IN HELIUM

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The investigation of the chemical kinetics and mechanisms of chemical reactions involving NO_2 and NO is conveniently conducted by checking their concentrations by means of electronic absorption spectra in the UV and visible regions. But quantitative measurements can be complicated by the tendency of both sides to associate. In form this manifests itself as a violation of the Beer-Lambert law. In this paper we examine anomalies of the UV spectrum of NO which arise in the presence of helium, a reagent often used as an inert carrier gas.

The UV spectra of gas phase NO has three characteristic peaks with maxima at 205, 215, and 226.5 nm (Fig. 1). The intensities of the edge peaks are virtually identical, while the middle peak is 20-30% higher. The magnitude of the optical density at the maximum absorption of the monomer form of NO ($D_m = D - D_d$) in the 3.5-64 torr (500-8500 Pa) pressure range varies proportionally with changes in pressure. The extinction coefficient of NO at 226.5 torr equals 33 liters/mole cm or, if it is estimated by $\varepsilon = D_m/Pl$, then it equals $1.8 \cdot 10^{-3} \text{ torr}^{-1} \text{ cm}^{-1} (1.35 \cdot 10^{-5} \text{ Pa}^{-1} \text{ cm}^{-1})$. At low pressure of NO (<500 Pa) the linear dependence of D_m on P_{NO} disappears [1].

In this same spectral range, the nitric oxide dimer absorbs over a broad spectral band [1]. Its maximum is located around 200 nm. The extinction coefficient of $(NO)_2$ is very high: at 226.5 nm it equals ~10⁴ liters/mole·cm, and at 205 nm it is three times greater. For this reason, absorption by the dimer is manifested by a rise in D_d with increasing P_{NO} (Fig. 1), despite its very low concentrations.

The UV spectral measurements were conducted on a UV-VIS Specord spectrometer using a D2E deuterium discharge lamp as a radiation source. All of the experiments were carried out at room temperature (~20°C) in a cell of length l = 5 cm, sealed into the circulation loop of a glass vacuum setup. The volume of the cell was about 20 ml, the volume of the loop being abut 400 ml. Its principal component is a glass circulation pump which assures a gas recirculation rate of ~10 liters/min. The diameter of the piping in the loop is 5 mm, and its length is 4 m. The quantity of gas introduced into the setup was measured by the pressure to within 70 Pa using a glass diaphragm, and compensated Burdon pressure gauges.

Experiments on the influence of He on the spectra of NO were carried out in several ways, each distinguished by the method in which the gas mixtures were prepared. Typically, to a specific quantity of NO, an increasingly greater quantity of He was added (tests Nos. 1–6 and 20–55), measuring the final pressure of the mixture following helium injection. Spectra were taken following mixing of the gases by the circulation pump. The pressure before and after mixing did not change. The results of tests Nos. 7–11 were obtained by successive removal of a portion of the gas mixture, beginning with experiment No. 6. The spectrum was taken following evacuation of the apparatus. Tests Nos. 12–19 were carried out with single dosages of the components. In these experiments each mix was prepared from new portions of NO and He. The results of these experiments agree well with previously measured values from measurements of the value of D_m at low values of P_{He} and P_{NO} . The experiments at the lowest NO pressure of 200 Pa (Nos. 56–59) were carried out by partial evacuation of the gas from test No. 55 with subsequent addition of new portions of He.

In this study, high-purity (hp) grade helium was used. Nitrogen oxide was obtained by reaction of a 40% $NaNO_2$ solution with a 1:1 by volume mixture of 20% $FeSO_4$ and 20% HCl solution. Passing through solid NaOH, it was purified and collected in a glass container with stopcocks at the entrance and exit. The process continued until the gas in the chamber was no longer discolored. The initial appearance of brown NO_2 is due to the presence of traces of air in the system. The purity of NO was checked by its white color upon freezing out on the liquid-nitrogen-cooled walls of the vessel. Degassing of the solid product allows for the ridding of trace N_2 from the sample. The presence of N_2 was verified chromatographically.

Mendeleev Institute of Chemical Technology, Moscow. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 53, No. 2, pp. 221–227, August, 1990. Original article submitted July 6, 1989.



Fig. 1. UV spectra of nitric oxide at P = 7660 Pa, without He (2) and with He at P = 59,000 Pa (3). 1) Absorption by empty cell (null line); D_d) absorption owing to the presence of the (NO)₂ dimer.

Fig. 2. Influence of the NO pressure on the increase of its absorption with various quantities of He (Pa): 1) 13,350; 2) 33,400; 3) 60,000.

Fig. 3. Increase in absorption by the $(NO)_2$ dimer in the presence of He as a function of the NO and He pressures. Results obtained over extended use of the UV radiation source (1, 2) and for a shorter irradiation time (3, 4): tests Nos. 41-47 (see Table 1) (5), 49 (6), and 34-39 (7); Nos. 13, 15, and 17 (8), 22-31 (9), 7-11 (10), and 2-6 (11).

Addition of helium to NO is capable of leading to a significant increase in the absorption by its monomer form (Fig. 1). Given $P_{NO} = \text{const}$, the dependence of the optical density D_m on the He concentration has an asymptotic character. The influence on He is most noticeable when it is present in great excess (by tens or hundreds of times (Table 1). All of the quantitative patterns in the change of the optical density of NO and (NO)₂ are exhibited by absorption at $\lambda = 226.5$

TABLE 1. Experimental Results of Measurement of the Optical Density of NO in Heliumat 226.5 nm

Number	Ptot.133.3 ⁻¹ Pa	PNO 133.3 ⁻¹ Pa	D	D _d
1 2 3 4 5 6 7 8 9 10 11	43,5 267 311 368 434 590 236,5 144,5 87,5 46,5 20	43,5 17,5 10,5 6,5 3,5 1,5	$\begin{array}{c} 0,565\\ 0,92\\ 0,965\\ 1,01\\ 1,06\\ 1,115\\ 0,61\\ 0,42\\ 0,3\\ 0,215\\ 0,17\\ \end{array}$	0,11 0,12 0,12 0,125 0,135 0,135 0,11 0,105 0,105 0,1 0,1
12 13 14 15 16 17 18 19	57,5 497,5 41,5 489 30,5 478,5 11 500	57,5 41,5 30,5 11	$\begin{array}{c} 0,705\\ 1,235\\ 0,56\\ 1,105\\ 0,44\\ 0,98\\ 0,235\\ 0,63\\ \end{array}$	0,12 0,16 0,115 0,145 0,11 0,145 0,1 0,11
20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38	$\begin{array}{c} 25,5\\57\\78,5\\101,5\\133,5\\182\\217,5\\274,5\\332\\425,5\\529\\617\\64\\79\\110,5\\180\\269\\345\\442\end{array}$	25,5 25,5 64	$\begin{array}{c} 0,38\\ 0,445\\ 0,535\\ 0,538\\ 0,648\\ 0,725\\ 0,775\\ 0,84\\ 0,9\\ 0,95\\ 0,772\\ 0,765\\ 0,83\\ 0,95\\ 1,075\\ 1,17\\ 1,28\end{array}$	$\begin{array}{c} 0,105\\ 0,105\\ 0,11\\ 0,11\\ 0,11\\ 0,11\\ 0,11\\ 0,11\\ 0,11\\ 0,115\\ 0,12\\ 0,135\\ 0,145\\ 0,11\\ 0,115\\ 0,12\\ 0,15\\ 0,175\\ 0,205\\ 0,235\end{array}$
39 40 41 42 43 44 45 46 47 48	535 15 36 99 176 247 343 435 536	15	1,235 0,28 0,305 0,41 0,495 0,56 0,635 0,685 0,74 0,185	0,265 0,1 0,1 0,11 0,115 0,125 0,14 0,155 0,16 0,1
49 50 51 52 53 54 55 56 57 58 59	3,5 15,5 53,5 113,5 222 335 424 504 200 251 351 484	1,5	0,105 0,29 0,215 0,26 0,295 0,335 0,355 0,365 0,2 0,21 0,215 0,225	0,1 0,1 0,105 0,105 0,11 0,11 0,115 0,105 0,105 0,105

Note. The magnitude of D was measured to an accuracy of 0.005. Experiments were implemented successively in accordance with their number: Nos. 1–19 were carried out over the course of another day. $D_0 = 0.1$ (the value of D for an empty cell).



Fig. 4. Influence of the pressure of He and NO on the relative increase of absorption by the monomer (notation for the experimental data is analogous to that of Fig. 3): tests with $P_{NO} > 530$ Pa (1), $P_{NO} = 470$ (2), and 200 Pa (3).

nm. Analogous changes take place at the other absorption maxima (205 and 215 nm). Increase of the optical density of NO due to the presence of $\text{He}[\Delta D = (D - D_d) - (D - D_d)_0$, where $(D - D_d)_0$ is the value of D_{NO} when $P_{\text{He}} = 0$] reaches 200% given a 30-fold excess of He. For commensurate quantities of He and NO the magnitude of ΔD is very small (~20%). The nature of the variation of ΔD with P_{He} is predetermined by the quantity of NO as well. When $P_{NO} > 500$ Pa, $\Delta D/D_{NO}$ as a function of P_{He}/P_{NO} is described by two successive straight lines with different slopes. Initially, when the ratio $P_{\text{He}}/P_{NO} < 8$, the values of the tangent of the slope angle amounts to 0.13, and subsequently to 0.04. For the case of low P_{NO} the first section practically vanishes and the second is observed directly afterwards.

The increase of absorption by NO in the presence of He (ΔD) is proportional to the product $(P_{NO} \cdot P_{He})^{0.5}$. For pressures ranging from 500 to 5300 Pa, the proportionality coefficient is independent of P_{NO} , being equal to 2.7.10⁻⁵ Pa⁻¹. At lower and higher NO concentrations, the proportionality coefficient decreases. The straight lines observed by plotting $\Delta D/P_{NO}^{0.5}$ vs. $P_{He}^{0.5}$, upon extrapolation to $\Delta D/P_{NO}^{0.5} = 0$, converge to a single point at which $P_{He} = 1600$ Pa. It is probable that a realistic function of $\Delta D/P_{NO}^{0.5}$ vs. $P_{He}^{0.5}$ is not linear at low He pressures. The rise in ΔD with increasing P_{NO} ceases when $P_{NO} = 5300$ Pa, independent of P_{He} (Fig. 2). Given a further increase in the amount of NO in the mixture, ΔD decreases. Results obtained indicate that absorption by monomeric NO in the presence of He has two sources, a usual one for which D is proportional to P_{NO} , and another arising due to the influence of He where ΔD is proportional to $(P_{NO} \cdot P_{He})^{0.5}$.

The He pressure also affects absorption by the dimer. Increase in the optical density of the dimer $\Delta D_d = D_d - (D_d)_0$, where $(D_d)_0$ is the value of D_d when $P_{He} = 0$, occurs in proportion to the product $(P_{He} P_{NO})$ (Fig. 3). Although the magnitude of ΔD_d is substantially less than ΔD , it may significantly exceed the initial values of $(D_d)_0$. In contrast with ΔD , the values of ΔD_d are not always satisfactorily reproducible. During operation of the deuterium lamp of the spectrometer, a clear tendency for ΔD_d to increase can be followed. For this reason, in the series of tests Nos. 20-31, a break in the linear dependence of $\Delta D_d/P_{NO}$ on P_{He} is observed in the segment containing the last two measurements (Nos. 30-31) where a more rapid increase in D_d is seen. Unfortunately, this phenomenon did not receive the necessary experimental correction, since at the time when the experiments were being carried out the phenomenon was not noted. In coordinates of log $(\Delta D_d/P_{He})$ vs. log P_{NO} all of the results can be plotted on two parallel lines; the upper one [log $(\Delta D_d/P_{He}) + 0.9 \log P_{NO} + 5 = 0$] describes the absorption intensity of the dimer during sustained operation of the equipment, while the other (with ΔD_d three to four times smaller) for less extended use of the equipment.

The patterns discovered in the changes in the optical density of the NO monomer upon addition of He indicate that the observed increase in absorption (ΔD) is due to the appearance of specific, apparently excited forms of nitric oxide, which form upon dissociation of the NO-He compound under the influence of UV radiation:

$$NO + He \stackrel{(1)}{\nleftrightarrow} NO \cdot He \stackrel{(2)}{\nleftrightarrow} (NO \cdot He)^* \stackrel{(3)}{\nleftrightarrow} (NO \cdot He)^{**} \stackrel{(4)}{\nleftrightarrow} NO^* + He^*$$
$$\uparrow \downarrow \stackrel{(5)}{\longrightarrow} NO^* + He^*$$

NO-inert gas compounds [2–5] belong to the set of clathrates [6]. They dissociate upon irradiation with emission of excited NO* molecules. The dependence of ΔD on P_{He} indicates that the equilibrium reaction (5) is virtually impossible to realize: $\Delta P_{NO*} = \Delta D/\epsilon_{NO*} l = (K_1 K_2 K_3 K_4)^{0.5} (P_{NO} P_{He})^{0.5}$, where K are the equilibrium constants of the corresponding reactions. Under conditions where P_{NO} = 500–5300 Pa, $(K_1 K_2 K_3 K_4)^{0.5} \epsilon_{NO*} = 0.001$ (cm·torr)⁻¹ = 7.5 ·10⁻⁶ Pa⁻¹cm⁻¹(I).

Undoubtedly, the UV spectrum of the NO monomer in the absence of He is to a significant degree due to the formation of its excited state via photolysis of the dimer.

$$NO + NO \stackrel{(6)}{\rightleftharpoons} (NO)_{2} \stackrel{(7)}{\rightleftharpoons} (NO)_{(2)}^{*} \stackrel{(8)}{\rightleftharpoons} (NO)_{2}^{*} \stackrel{(9)}{\rightleftharpoons} NO^{*} + NO^{*}$$

$$\downarrow \downarrow (10) \\ NO^{*} + NO$$

The observed dependence of D_d on P_{NO}^2 excludes from consideration reaction (10). If such a dissociation of $(NO)_2^*$ was to occur, then the proportionality coefficient between log D_d and log P_{NO} would be smaller. From the slope of the line $D_{NO} = f(P_{NO})$, it follows that $(K_6K_7K_8K_9)^{0.5} \epsilon_{NO^*} = 0.0019 \text{ (cm-torr)}^{-1} = 14.2 \cdot 10^{-6} \text{ Pa}^{-1} \text{ cm}^{-1}$ (II).

Using the known values $K_6 = 1.5 \cdot 10^{-18} \text{ mm}^{-1}$ [1], we obtain $\epsilon_{NO^*} = 16/(K_7 K_8 K_9)^{0.5} \text{ cm}^{-1} \cdot \text{torr}^{-0.5} = (1.34/K_7 K_8 K_9)^{0.5} \text{ cm}^{-1} \cdot \text{Pa}^{-0.5}$ (III). Distortion of the linear dependency at low NO pressures (<500 Pa) [1] is due, apparently, to known changes in the reaction order of the homolytical thermal decay of substances in these conditions from the first to the second steps [7]. In this case, $P_{NO^*} = K_6^{0.25} (K_7 K_8 K_9)^{0.5} \cdot P_{NO}^{0.5}$.

A combined examination of the two formation paths of NO; from $(NO)_2$ and NO He permits the results of all of the tests where $P_{NO} > 500$ Pa to be described by a single straight line when plotted in terms of $\Delta D/D_{NO}$ vs. $(P_{He}/P_{NO})^{0.5}$. The tangent angle of its slope equals $(K_1K_2K_3K_4/K_6K_7K_8K_9)^{0.5} = 0.5$. From which it follows that $K_1K_2K_3K_4/K_6K_7K_8K_9)$ = 0.25 (IV). The ratio obtained indicates that, under the influence of He, nitric oxide is less likely to convert to an excited state than to convert via self-association. From the similarity of the processes (6) and (9) (1) and (4), it follows that K_1/K_6 = K_9/K_4 and $K_1K_4 = K_6K_9$ (V). Taking into account this equality, from the ratio (III) we obtain $K_7K_8/K_2K_3 = 4$ (VI), i.e., the dimer (NO)₂ is more readily subject to photolysis than NO He.

The appearance of a maximum in the function $\Delta D = f(P_{NO})$ (Fig. 2) may be due to association of NO-He with NO leading to formation of $(NO)_2$ He. But for such a conversion scheme, it is necessary that ΔD_d be proportional to P_{NO}^2 . In actuality, this is hardly the case. Apparently, absorption by the dimer, as with the monomer, is due to the appearance of its excited forms. In the presence of He, it forms predominantly by association of an excess quantity of NO* as a result of the equilibrium equations (1)-(4), (9). For the mechanism under consideration, $P_{NO*} = (K_1K_2K_3K_4)^{0.5} (P_{NO} P_{He})^{0.5} - 2/K_9(\Sigma P_{NO*}^2 - P_{NO*}^2)$, where ΣP_{NO*} is the NO* pressure with He present, and P_{NO*} is the NO* pressure in the absence of helium. From this, it follows that $D^2 - D_{NO}^2 = (K_9 \varepsilon_{NO*}) (0.125 P_{NO}^{0.5} - \Delta D)$. Available experimental data is well described by the function, yielding $K_9 \varepsilon_{NO*} = 0.6 \text{ cm}^{-1}$ (VII). Substituting (VII) into expression (III), we obtain $K_7 K_8/K_9 = 600 \text{ tor } = 4.5 \text{ Pa}^{-1}$ (VIII). The magnitude of this ratio indicates that the dimer is easily excited upon irradiation, and the concentration of its excited states is commensurate with the unexcited component.

The increase in ΔD_d with the lengthening of the deuterium lamp operation time may be due to the presence of two excited states of the dimer with different absorptoins: $\varepsilon_{(NO)2^*} > \varepsilon_{(NO)2^{**}}$. In the specified conditions, equilibrium between them is capable of substantially shifting toward the (NO)₂ side, a result of which is a growth in D_d (Fig. 3). In the following case, $K_8^* < K_8$.

Proceeding from $D_d = D_{(NO)2^*} + D_{(NO)2^{**}} = (P_{(NO)2^*} \varepsilon_{(NO)2^*} + P_{(NO)2^{**}\varepsilon_{(NO)2^{**}}}) \cdot l$ and taking into account that in the presence of He $P_{(NO)2^*} = P_{NO^*}^2/K_8 K_9$ and $P_{(NO)2^{**}} = P_{NO^*}^2/K_9$, we have $D_d = (\Sigma P_{NO^*}^2/K_9)(\varepsilon_{(NO)2^*}/K_8 + \varepsilon_{(NO)2^{**}}) \cdot l$ and $\Delta D_d = (K_1 K_2 K_3 K_4/K_9) \cdot P_{NO^*} P_{He'}(\varepsilon_{(NO)2^*}/K_8 + \varepsilon_{(NO)2^{**}}) \cdot l$. For a minimum slope of the linear function, $\Delta D_d = f(P_{NO^*} P_{He})$, we obtain $(K_1 K_2 K_3 K_4/K_9)(\varepsilon_{(NO)2^*}/K_8 + \varepsilon_{(NO)2^{**}}) = 0.11 \cdot 10^{-10} \text{ cm}^{-1} \cdot Pa^{-2}$ (IX). When the slope is a maximum, this same expression equals $0.85 \cdot 10^{-10} \text{ cm}^{-1} \cdot Pa^{-2}$. Their difference will be $(K_1 K_2 K_3 K_4/K_9) \cdot \varepsilon_{(NO)2^{**}} (1/K_8^* - 1/K_8) = 0.74 \cdot 10^{-10} \text{ cm}^{-1} \cdot Pa^{-2}$ (X). The straight lines in coordinates of $D_d - D_m^{-2}$, on the basis of the expression $D_d/D_m^2 = (1/\varepsilon_{NO^*}^2 \cdot K_9 \cdot l)(\varepsilon_{(NO)2^*}/K_8 + \varepsilon_{(NO)2^{**}})$ (XI), give for a minimum slope $(1/\varepsilon_{NO^*})(\varepsilon_{(NO)2^*}/K_8 + \varepsilon_{(NO)2^{**}}) = 0.13$, and for a maximum 0.48. Their difference is $(\varepsilon_{(NO)2^*}/\varepsilon_{NO^*})(1/K_8^* - 1/K_8) = 0.35$ (XII).

Based on the derived relations, it is possible to find the value of $\varepsilon_{NO}^* = 0.7 \text{ (cm-torr)}^{-1} = 5 \cdot 10^{-3} \text{ (cm-Pa)}^{-1}$ selectable. Then $K_9 = 0.9$ torr = 120 Pa, $K_7K_8 = 660$, $K_2K_3 = 165$, $K_6K_9 = K_1K_4 = 1.3 \cdot 10^{-8}$. When the equilibrium (8) shifts toward $(NO)_2^{**}$, $K_8 > K_7$. In the opposite case, $K_7 \ge K_8$. Such a case is possible if $\varepsilon_{(NO)_2^{**}} \approx \varepsilon_{NO^*}$. Then the right-hand side of expression (XI) is determined primarily by the magnitude of $\varepsilon_{(NO)_2^{**}} \approx 0.1 \text{ (cm-torr)}^{-1} = 0.75 \cdot 10^{-3} \text{ (cm-Pa)}^{-1}$. If one turns to the value $K_8 \approx 70$, then $K_7 \approx 10$ and $K_8^* \approx 3$. Available results do not allow for one to obtain definitive values of K_1 and K_4 , because they do not bear direct information on the concentration of the NO-He compound. Typically, the stability of clathrates is lower than that of compounds which form by chemical bonds. For this reason one ought to expect that $K_4 > K_9$ and, correspondingly, $K_1 < K_6$. If one takes $K_4 \approx 10$ torr = 1335 Pa, then K_1 will equal $10^{-9} (\text{torr})^{-1} = 7.5 \cdot 10^{-12} \text{ Pa}^{-1}$.

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INVESTIGATION OF ELECTRONIC SPECTRA OF SOME POLY(ORGANOSILOXANES)

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The luminescence of siloxane polymers containing phenyl groups has been studied very inadequately [1], although such polymers are widely used as protective coatings under exposure to UV and ionizing radiation. The kinetic dependences of the luminescence of siloxanes during various stages of photophysical processes have not been studied previously. The effect of acceptor-type additives, the polycyclic aromatic hydrocarbons anthracene, phenanthrene, and fluorene, and their organosilicon analogs, on the photolysis and radiolysis of ring-chain poly(methylphenylsiloxanes) has been investigated [2, 3].

It was shown that the introduction of siloxodihydrophenanthrenyl (PA) structural repeating units and phenanthrene into poly(organosiloxanes) exerts a significant stabilizing effect because such additives have low-lying excitation levels and are therefore able to scatter a significant part of the absorbed energy without cleavage of chemical bonds in radiative and (or) radiationless transitions. Therefore, it seemed of interest to consider fluorescence and phosphorescence spectra of some poly(methylphenylsiloxanes) containing PA repeating units and to compare the phosphorescence spectra obtained by steady-state luminescence spectroscopy and luminescence of PA repeating units in block copolymers under pulsed photoexcitation by radiation with $\lambda = 308$ nm.

We investigated ring-chain methylphenylsiloxane oligomers (PMPS) synthesized by hydrolytic polycondensation in toluene containing 2.5 mole % PA repeating units with the general formula



M. V. Lomonosov Moscow State University. Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 53, No. 2, pp. 228-232, August, 1990. Original article submitted July 20, 1989.

UDC 541.14+541.15