

Matrix Isolation Infrared Spectra of Hydrogen Halide and Halogen Complexes with Nitrosyl Halides

Donald Lucas,* Louis J. Allamandola**, and George C. Pimentel

Department of Chemistry University of California Berkeley, California 94720

Received December 29, 1981

Matrix isolation infrared spectra of nitrosyl halide (XNO) complexes with HX and X₂ (X = Cl, Br) are presented. The relative frequency shifts of the HX mode are modest (ClNO·H—Cl, $\Delta\nu/\nu = -0.045$; BrNO·H—Br, $\Delta\nu/\nu = -0.026$), indicating weak hydrogen bonds 1–3 kcal/mol. These shifts are accompanied by significant shifts to higher frequencies in the XN—O stretching mode (ClN—O·HCl, $\Delta\nu/\nu = +0.016$; BrN—O·HBr, $\Delta\nu/\nu = +0.011$). Similar shifts were observed for the XN—O·X₂ complexes (ClN—O Cl₂, $\Delta\nu/\nu = +0.009$; BrN—O—Br₂, $\Delta\nu/\nu = +0.013$). In all four complexes, the X—NO stretching mode relative shift is opposite in sign and about 1.6 times that of the NO stretching mode.

These four complexes are considered to be similar in structure and charge distribution. The XN—O frequency shift suggests that complex formation is accompanied by charge withdrawal from the NO bond ranging from about .04 to .07 electron charges. The HX and X₂ molecules act as electron acceptors, drawing electrons out of the antibonding orbital of NO and strengthening the XN—O bond. The implications of the pattern of vibrational shifts concerning the structure of the complexes are discussed.

INTRODUCTION

Because of the unusual bonding implied by the molecular structures of the nitrosyl halides — their relatively long halogen-nitrogen and short nitrogen-oxygen bond lengths¹ — they have attracted considerable interest. The rather different explanations^{2–5} ask for new types of information to provide additional insight concerning the nature of these interesting molecules. With this incentive, we have investigated the matrix isolation infrared spectra of the complexes formed by the nitrosyl halides with hydrogen halides and with halogens. The hydrogen halides offer a useful reference since the frequency shift of the HX stretching mode in a hydrogen bonded complex correlates with the bond dissociation energy^{6–8}. The halogens were selected because of the startling observation by Hisatsune and Miller⁹ that the ν_{11} band of ClNO (the N—O stretching mode) is shifted by +150 cm⁻¹ when ClNO is trapped in solid chlorine. The magnitude and direction of the shift suggest than an ion pair,

* Present Address: Energy and Environment Division, Lawrence Berkeley Laboratory, University of California at Berkeley, Berkeley, California 94720.

** Present Address: Laboratory AstroFysica, Huygens Laboratorium-Wassenaarweg 78, Leiden 2405 Nederland

* Festschrift of Professor Dušan Hadži.

$\text{NO}^+ \cdot \text{Cl}_3^-$, may be formed and they indicate that the N—O stretching frequency responds sensitively to complex formation.

We report here the matrix infrared spectra of the complexes $\text{ClNO} \cdot \text{HCl}$, $\text{ClNO} \cdot \text{Cl}_2$, $\text{BrNO} \cdot \text{Br}_2$, and $\text{BrNO} \cdot \text{HBr}$ ^{10,11}.

EXPERIMENTAL

The matrix samples were prepared by pulsed deposition¹²⁻¹⁴ in a 2 to 4 hour period using solenoid-automated equipment pioneered by Allamandola¹⁴ and developed by Lucas¹¹. Approximately 8 to 20 millimoles of sample were deposited onto a CsI window held at 20K; pulses of ~ 3 micromoles of gas mixture per pulse (M/R ranging from 100 to 600) at a two pulse per minute rate were used. Spectra were recorded with a Beckman IR-7 spectrophotometer with NaCl and CsI optics over the spectral range 300 to 4000 cm^{-1} . Spectral slit widths were about 3 cm^{-1} in the range 1800 to 2600 cm^{-1} and 4–6 cm^{-1} at 600 cm^{-1} . Frequency accuracies are about ± 2 cm^{-1} .

The matrix gas, N_2 , was passed through a copper coil immersed in liquid N_2 prior to use. The ClNO , Cl_2 , and Br_2 were solidified to eliminate dissolved air and then vaporized, a middle fraction being accepted for sample preparation.

RESULTS

$\text{ClNO} \cdot \text{HCl}$

The dotted line in Figure 1. shows the infrared spectrum of HCl in solid nitrogen ($\text{N}_2/\text{HCl} = 350$) in the spectral region 2600–3000 cm^{-1} . The solid line superimposed is the spectrum recorded when ClNO is also present ($\text{N}_2/\text{ClNO}/\text{HCl} = 350/1/1$). The features common to both spectra, 2854 cm^{-1} and 2810 cm^{-1} , are known to be due to absorption by HCl monomers and dimers, respectively¹⁵. The broad feature at 2726 cm^{-1} (O. D. = 0.11; half-width $\Delta\nu_{1/2} \sim 50$ cm^{-1}) is readily attributed to the $\text{ClNO} \cdot \text{HCl}$ complex with a relative shift $\Delta\nu/\nu = -0.045$. When DCl is used, the monomeric DCl feature

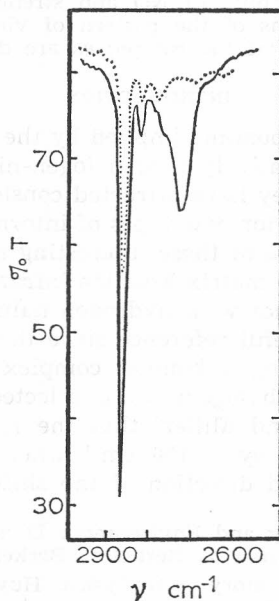


Figure 1. Infrared Spectrum of $\text{ClNO} \cdot \text{HCl}$ in N_2 , 2600–2950 cm^{-1} , at 20K: $\text{N}_2/\text{HCl} = 350$; — $\text{N}_2/\text{ClNO}/\text{HCl} = 350/1/1$.

at 2064 cm^{-1} is shifted to 1977 cm^{-1} ($\Delta\nu_{1/2} \sim 10\text{ cm}^{-1}$). Despite the different band widths, the relative shift of the DCl absorption, $\Delta\nu/\nu = -0.042$, shows that the 2726 and 1977 cm^{-1} features can be assigned to the hydrogen halide stretching motion in a complex with ClNO.

Figure 2. shows the spectral regions 1800 to 1900 and 550 to 600 cm^{-1} . In this figure, the dotted lines shown the spectrum of ClNO in N_2 ($\text{N}_2/\text{ClNO} = 1500$) while the solid lines show the spectrum when HCl is also present ($\text{N}_2/\text{ClNO}/\text{HCl} = 1500/1/5$). The dotted spectra include absorptions due to ClNO at 1833 cm^{-1} (0.46) and 582 cm^{-1} (0.12), to be compared to the gas phase frequencies 1799 cm^{-1} (ν_1)₋₁ and 605 cm^{-1} (ν_3)¹⁶. Absorption by ClNO was also recorded at 322 cm^{-1} (0.06) (gas phase $\nu_2 = 265\text{ cm}^{-1}$) but under such poor spectral conditions due to atmospheric absorptions that the spectra have little diagnostic value. The dotted spectrum also includes absorptions at 1876 cm^{-1} (0.14) and 1867 cm^{-1} (0.14) due to NO monomer and dimer^{11,17}. When HCl is also present, new absorptions appear at 1863 cm^{-1} (0.12; $\Delta_{1/2} = 15\text{ cm}^{-1}$) and 567 cm^{-1} (0.06; $\Delta_{1/2} = 5\text{ cm}^{-1}$). The proximity to ClNO absorptions readily identifies the new features as ν_1 and ν_3 of ClNO in the ClNO · HCl complex with relative shifts, respectively, of $+0.016$ and -0.026 .

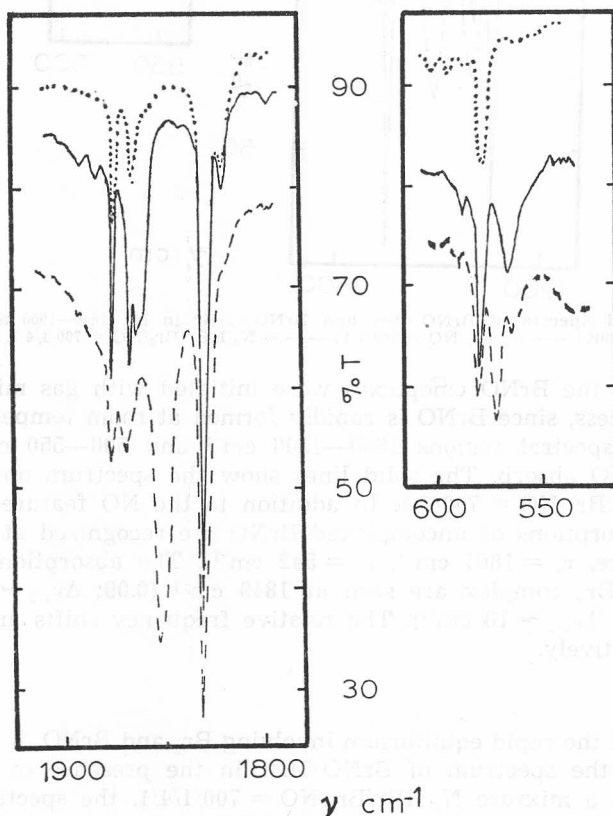


Figure 2. Infrared Spectra of ClNO · HCl and ClNO · Cl₂ in N₂, 1800–1900 and 550–600 cm⁻¹, 20K: N₂/ClNO=1500; — N₂ClNO/HCl = 1500/1/1; - - - N₂/ClNO/Cl₂ = 700/1/5.

ClNO · Cl₂

The dashed spectrum in Figure 2. refers to a sample containing Cl₂ and ClNO ($N_2/ClNO/Cl_2 = 700/1/5$). New absorptions attributable to the ClNO · Cl₂ complex are obvious at 1850 cm⁻¹ (0.28; $\Delta\nu_{1/2} = 18$ cm⁻¹) and 572 cm⁻¹ (0.02; $\Delta\nu_{1/2} = 5$ cm⁻¹). The relative frequency shifts, $\Delta\nu/\nu$, are, respectively, +0.0093 and -0.017, qualitatively similar to those of the ClNO · HCl complex. It is possible that the weak absorption at 560 cm⁻¹ (0.04) is due to Cl₂ in ClNO · Cl₂ since the Cl₂ gas phase frequency is 557 cm⁻¹, and the Cl₂ absorption has been observed by Fredin and Nelander¹⁸ in a number of weak chlorine complexes.

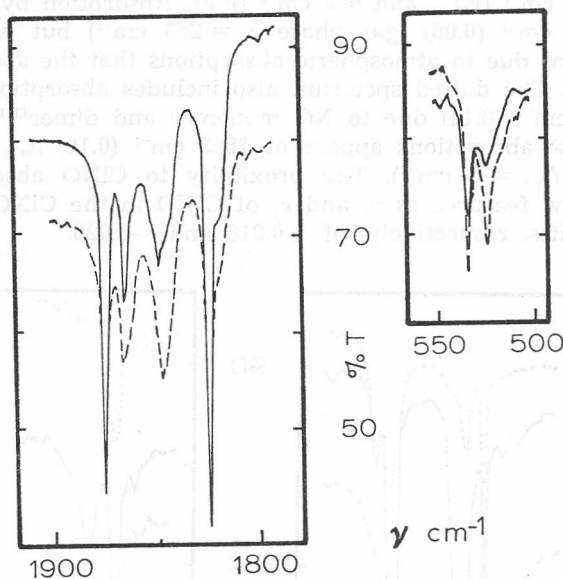
BrNO · Br₂

Figure 3. Infrared Spectra of BrNO · Br₂ and BrNO · HBr in N₂, 1800—1900 and 550—600 cm⁻¹, 20K: — N₂/Br₂/NO = 700/4/1; --- N₂/HBr/Br₂/NO = 700/1/4/1.

Studies of the BrNO complexes were initiated with gas mixtures of NO and Br₂ in excess, since BrNO is rapidly formed at room temperature. Figure 3. shows the spectral regions 1800—1900 cm⁻¹ and 500—550 cm⁻¹ where ν_1 and ν_3 of BrNO absorb. The solid lines show the spectrum obtained from a mixture of N₂/Br₂/NO = 700/4/1. In addition to the NO features at 1876 and 1867 cm⁻¹, absorptions of uncomplexed BrNO are recognized at 1825 and 534 cm⁻¹ (gas phase, $\nu_1 = 1801$ cm⁻¹, $\nu_3 = 542$ cm⁻¹). The absorptions attributable to the BrNO · Br₂ complex are seen at 1849 cm⁻¹ (0.09; $\Delta\nu_{1/2} \sim 20$ cm⁻¹) and 525 cm⁻¹ (0.04, $\Delta\nu_{1/2} \sim 10$ cm⁻¹). The relative frequency shifts are +0.013 and -0.017, respectively.

BrNO · HBr

Because of the rapid equilibrium involving Br₂ and BrNO, it was necessary to search for the spectrum of BrNO · HBr in the presence of the BrNO · Br₂ complex. With a mixture N₂/HBr/Br₂/NO = 700/1/4/1, the spectrum shown as a dashed line in Figure 3 is obtained. With the conventional spectral slit width, the spectrum qualitatively resembles that of BrNO · Br₂. However, with

narrower spectral slits and slower scan rates, the feature near 1850 cm^{-1} is seen to consist of three peaks at 1844, 1847, and 1849 cm^{-1} . Since the $\text{BrNO}\cdot\text{Br}_2$ complex absorbs at 1849 cm^{-1} , the other features are assigned to $\text{BrNO}\cdot\text{HBr}$. No distinctive feature near 525 cm^{-1} could be discerned that might be attributed to this complex; it is presumed to be masked by coincidence with absorption by $\text{BrNO}\cdot\text{Br}_2$. The spectral region $2400\text{--}2600\text{ cm}^{-1}$, in which the HBr stretching mode is found, also involved overlapping features. The absorptions at 2545 and 2495 cm^{-1} , attributable to HBr monomer and dimer, were accompanied in the $\text{HBr}/\text{Br}_2/\text{NO}$ experiment by a broad shoulder near 2480 cm^{-1} that is attributed to the complex. Clearly, our ability to determine the $\text{BrNO}\cdot\text{HBr}$ infrared spectrum is compromised somewhat by the inevitable presence of an interference by $\text{BrNO}\cdot\text{Br}_2$.

We tentatively assign 2480 , $1844\text{--}7$, and 525 cm^{-1} to $\text{BrNO}\cdot\text{HBr}$ with relative frequency shifts, respectively, of -0.026 , $+0.011$, and -0.017 .

Table I summarizes the assigned frequencies and relative frequency shifts for these four complexes.

TABLE I

Absorption Frequencies and Relative Frequency Shifts for XNO Complexes with X_2 and HX in Solid N_2

	ν_1 (cm^{-1})	ν_3 (cm^{-1})	ν_{HX} (cm^{-1})	$\frac{\Delta\nu_1}{\nu_1}$	$\frac{\Delta\nu_3}{\nu_3}$	$\frac{\Delta\nu_{\text{HX}}}{\nu_{\text{HX}}}$
$\text{ClNO}\cdot\text{Cl}_2^{\text{a}}$	1850	572	—	+0.0093	—0.017	—
$\text{ClNO}\cdot\text{HCl}^{\text{b}}$	1863	567	2726	+0.16	—0.026	—0.045
$\text{BrNO}\cdot\text{Br}_2^{\text{c}}$	1849	525	—	+0.013	—0.017	—
$\text{BrNO}\cdot\text{HBr}^{\text{d}}$	1844, 1847	(525)	2480	+0.010, 0.012	(—0.017)	—0.026

^a ClNO in N_2 , $\nu_1 = 1833\text{ cm}^{-1}$, $\nu_3 = 582\text{ cm}^{-1}$

^b HCl in N_2 , $\nu_{\text{HCl}} = 2854\text{ cm}^{-1}$

^c BrNO in N_2 , $\nu_1 = 1825\text{ cm}^{-1}$, $\nu_3 = 534\text{ cm}^{-1}$

^d HBr in N_2 , $\nu_{\text{HBr}} = 2545\text{ cm}^{-1}$

DISCUSSION

The relative frequency shifts in Table I show obvious correlation. Table II displays this correlation through the ratios of the relative frequency shifts. In the hydrohalide complexes the relative shift of the HX stretching mode is opposite in sign and 2—1/2 times as large as the relative shift of the NO stretching mode. In all four of the complexes, the X—N stretching mode relative shift is opposite in sign and about 1.6 times that of the NO stretching mode. The approximate constancy of these ratios suggests similarity in the structures of these complexes as well as a systematic charge redistribution that reflects into the bonds of the parent molecules.

Clues to the nature of the bonding and charge redistribution in the complexes are provided by the HX and the NO frequency shifts. The former can be compared to $\Delta\nu_{\text{HCl}}/\nu_{\text{HCl}} = -0.11$ in the dimethyl ether complex¹⁹ with bond energy 7.1 kcal/mol^{20} . The much smaller values of $\Delta\nu_{\text{HX}}/\nu_{\text{HX}}$ suggest hydrogen bond energies in the range $1.5\text{--}3\text{ kcal/mol}$. The same qualitative result is obtained using the vibrational correlation diagram of AULT and coworkers¹⁹

to derive proton affinities: for ClNO, P. A. ≈ 70 kcal and for BrNO, P. A. ≈ 35 kcal (compare P. A. of H₂O, 163 kcal). Thus the frequency shifts $\Delta\nu_{\text{HX}}/\nu_{\text{HX}}$ are characteristic of quite weak hydrogen bonded complexes.

The NO frequency shifts can be attributed to charge redistribution in the XNO molecule. In a variety of NO complexes and MNO compounds^{3,5} the NO vibrational frequency has been taken to be a measure of antibonding molecular orbital occupancy and, hence, the bond order. In NO, this M. O. is half-occupied, giving a 2—1/2 order bond (and $\nu = 1876$ cm⁻¹). In NO⁺, the antibonding orbital is empty, so the bond becomes a triple bond while in NO⁻, it is doubly occupied to provide a double bond. Evidence has been compiled that indicate that NO⁺ absorbs at ~ 2240 cm⁻¹^{21,22}, while the NO⁻ absorption is at ~ 1350 cm⁻¹^{23,24}. These tie points furnish an estimate of the direction and amount of charge movement as the XNO complexes form. Since the shifts observed are towards higher frequencies, charge is being removed from the NO group in amount ranging from 0.07 electron removal in ClNO·HCl to about half that in ClNO·Cl₂. The two BrNO complexes fall between, with charge removal of 0.04 electron in BrNO·HBr and 0.05 electron in BrNO·Br₂.

It is not immediately obvious at which end of XNO the complex formation is to be expected. If HX and X₂ were to attach to the halogen end of the XNO molecule, charge removal from NO might signify incipient formation of HX₂⁻NO⁺ and X₃⁻NO⁺ ion pairs. This would produce the pattern of frequency shifts observed. However, there is evidence to suggest that the charge distribution in the XNO molecules does not encourage such a molecular geometry. The NO vibrational frequencies in both ClNO and BrNO are shifted downward relative to that of NO. These frequency shifts suggest that there is a transfer of about 0.12 to 0.14 electron from the halogen atom to the NO group in both ClNO and BrNO. This model implies that these two molecules should have substantial dipole moments, about 1.4D for ClNO and 1.7D for BrNO. The measured values of the dipole moments, 1.86D for ClNO and 1.80D for BrNO²⁵, agree well with this prediction. It should be noted that the dipole moment of NO itself is quite small, 0.15D. In the complexes with HX, the XNO molecule is expected to act as an electron donor, so bond formation at the negative NO group would be plausible. As an electron acceptor, the HX molecule would tend to draw charge out of the NO group, the direction indicated by $\Delta\nu_{\text{NO}}/\nu_{\text{NO}}$. Klemperer et al., in their studies of van der Waals complexes of the halogens²⁶, argue that ClF also acts as an electron acceptor. By analogy, Cl₂ would also tend to seek the negatively charged NO group in the XNO·X₂ complexes and, hence, remove charge from the NO antibonding orbital, raising ν_{NO} , as observed. Any tendency to remove charge from the NO group could be expected to weaken somewhat the X—N bonds at the other end of the molecule. Thus the pattern of frequency shifts indicates removal of charge from the NO bond but does not decisively show at which end of the molecule the complex forms.

CONCLUSION

The observations presented in Table I and II show that the frequency shifts in the XNO·HX and XNO·X₂ complexes link them in bonding type. They are found to be relatively weak complexes, 1.5—3 kcal/mol, in which the strengthening of the NO bonds and weakening of the X—N bonds are

TABLE II

Ratios of the Relative Frequency Shifts in the XNO Complexes with X₂ and HX in Solid N₂

	$\frac{\Delta\nu_{\text{HX}}/\nu_{\text{HX}}}{\Delta\nu_{\text{XN-O}}/\nu_{\text{XN-O}}}$	$\frac{\Delta\nu_{\text{X-NO}}/\nu_{\text{X-NO}}}{\Delta\nu_{\text{XN-O}}/\nu_{\text{XN-O}}}$
CINO · HCl	— 2.81	— 1.63
BrNO · HBr	— 2.38	— 1.56
average	— 2.6 ± .2	— 1.60 ± .04
CINO · Cl ₂	—	— 1.85
BrNO · Br ₂	—	— 1.31
average	—	— 1.58 ± .4

connected with removal of charge from the NO group. The anticipated sensitivity of the NO stretching frequency is indeed evident, but the 150 cm⁻¹ frequency shift shown by CINO in solid Cl₂,⁹ is reduced tenfold when CINO · Cl₂ is formed in solid nitrogen. The larger frequency shift, which corresponds to removal of about one third of an electron charge, might indicate a concerted effect at both ends of the molecule when CINO is enclosed in a Cl₂ matrix cage.

Acknowledgement. — We gratefully acknowledge research support from the National Aeronautics and Space Administration Grant No. NGL-05-003-286.

REFERENCES

1. FNO: D. W. Magnuson, *J. Chem. Phys.* **19** (1951) 1071; CINO: W. G. Burns and H. J. Bernstein, *J. Chem. Phys.* **18** (1950) 1669; BrNO: T. L. Weatherly and Q. Williams, *J. Chem. Phys.* **25** (1956) 717.
2. L. Pauling, *The Nature of the Chemical Bond*, Third Ed., Cornell Univ. Press., Ithaca, N. Y. (1960), p. 345—6.
3. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, New York, N. Y. (1966), p. 356.
4. J. W. Linnett, *The Electronic Structure of Molecules*, Wiley & Sons, N. Y. (1964), p. 78—80.
5. R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.* **88** (1966) 2394.
6. G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman & C., San Francisco, Calif. (1960), p. 82—86.
7. G. C. Pimentel and A. L. McClellan, *Ann. Rev. Phys. Chem.* **22** (1971) 347.
8. D. Hadži and S. Bratos, Ch. 12. *Vibrational Spectroscopy of the Hydrogen Bond*, *The Hydrogen Bond*, Vol. II, ed. P. Schuster, G. Zundel, and C. Sandorfy, North Holland Pub. Co., Amsterdam (1975).
9. I. C. Hisatsune and P. Miller, Jr., *J. Chem. Phys.* **38** (1963) 49.
10. Other complexes were studied, but with less definitive assignments because of overlapping bands: BrNO · HCl, CINO · Br₂, and BrNO · Cl₂, see ref. 11.
11. D. Lucas, *Ph. D. Dissertation*, University of California, Berkeley, 1977.
12. M. M. Rochkind, *Anal. Chem.* **39** (1967) 567; **40** (1968) 762.
13. R. N. Perutz and J. J. Turner, *Trans. Faraday Soc.* **II** **4**, 452 (1973).
14. L. Allamandola, *Ph. D. Dissertation*, University of California, Berkeley, 1974.
15. A. J. Barnes, H. E. Hallam, and G. F. Scrimshaw, *Trans. Faraday Soc.* **65** (1969) 3150.
16. L. Landau, *J. Molec. Spect.* **4** (1960) 276.
17. E. L. Varetti and G. C. Pimentel, *J. Chem. Phys.* **55** (1971) 3813.
18. L. Fredin and B. Nelander, *Mol. Phys.* **27** (1974) 885.
19. B. Ault, E. Steinback, and G. C. Pimentel, *J. Phys. Chem.* **76** (1975) 615.

20. G. Govil, A. D. H. Clague, and H. J. Bernstein, *J. Chem. Phys.* **49** (1968) 2821.
21. W. L. S. Andrews and G. C. Pimentel, *J. Chem. Phys.* **44** (1966) 2361.
22. D. W. A. Sharp and J. Thorley, *J. Chem. Soc.* 3557 (1963).
23. D. E. Milligan and M. E. Jacox, *J. Chem. Phys.* **55** (1971) 3404.
24. D. E. Teavault and L. Andrews, *J. Phys. Chem.* **77** (1973) 1646.
25. A. L. McClellan, *Tables of Experimental Dipole Moments*, Rahaara Enterprises (1974).
26. S. E. Novick, K. C. Janda, and W. Klemperer, *J. Chem. Phys.* **65** (1976) 5115.

IZVLEČEK

Infrardeči spektri simetrično izoliranih aduktov med nitrozilovimi halogenidi in vodikovimi halogenidi ali halogeni

Donald Lucas, Louis J. Allamandola in George C. Pimentel

Nitrozilovi halogenidi (XNO) so zanimivi zaradi nenavadnih vezi, ki jih kaže njihova molekulska struktura: razdalja med atomi halogena in dušika je razmeroma velika, razdalja med dušikom in kisikom pa razmeroma majhna. Raziskani so infrardeči spektri aduktov teh spojin z vodikovimi halogenidi, XNO·HX, in halogeni, XNO·X₂ (X = Cl, Br), izoliranih v matrikah trdnega dušika. Relativni premiki frekvenc pri nihanjih ν XH so majhni, saj imamo $\Delta\nu/\nu = -0,045$ za ClNO·HCl in $\Delta\nu/\nu = -0,026$ za BrNO·HBr. To kaže, da so ustrezne vodikove vezi šibke, in sicer od 1.5 do 3 kcal/mol. Te premike pa spremljajo pomembni premiki frekvence valenčnega nihanja XN—O proti višjim valovnim številom. Tako dobimo $\Delta\nu/\nu = +0,016$ za ClO—O·HCl in $\Delta\nu/\nu = 0,021$ za BrN—O·HBr. Podobne premike opazimo za komplekse XNO·X₂, pri čemer je $\Delta\nu/\nu = +0,009$ za ClN—O·Cl₂ in $\Delta\nu/\nu = +0,013$ za BrN—O·Br₂. Pri vseh štirih kompleksih pa najdemo relativni premik valenčnega nihanja X—NO z nasprotnim predznakom in približno 1,6 krat večji od valenčnega nihanja N—O.

Lahko sklepamo, da imajo ti štirje kompleksi podobno strukturo in porazdelitev nabojev. Premik frekvence X—N—O kaže na to, da se pri tvorbi kompleksa približno 0,04 do 0,07 elektronskih nabojev »izvleče« iz N—O vezi. Molekule HX in X₂ delujejo kot elektronski akceptorij, ki vlečejo elektrone iz protivezne orbitale NO in ojačijo vez XN—O. Pri tem se verjetno vez X—N nekoliko oslabi, ni pa očitno, na katerem koncu molekula tvori kompleks.