Vibrational Assignments for Methyl Nitrite Rotamers

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Summary Vibrational and electronic spectra of methyl nitrite (H_3CONO and D_3CONO) have been recorded for both vapour-phase and matrix-isolated samples; by means of a photochemical effect, complete assignment of fundamental vibrations for each rotamer has been achieved.

The isomerism of covalent nitrites, X–O–N=O, is of interest, because as well as structural isomers ($X–NO_2$, nitro-compounds) rotational isomers[1] (rotamers), described as *s-transoid* or *s-cisoid* (or possibly *gauche*), also exist. For nitrous acid[2] the *s-transoid* rotamer is more stable, by 2·1 kJ mol^{-1}, than the *s-cisoid* rotamer. For methyl nitrite, despite several studies[3] of vibrational, electronic, and ^1H n.m.r. spectra, some questions remain unanswered, although a study[4] of the microwave spectra of both rotamers has established relative stability and values for rotational constants and dipole moments. In this case, the *s-cisoid* rotamer is the more stable,[4] by *ca.* 3·3 kJ mol^{-1}; dipole moments are (6·84 ± 0·10) and (7·86 ± 0·07) × 10^{-30} C m for *s-cisoid* and *s-transoid* rotamers, respectively. We have identified the vibrational fundamentals of each rotamer unambiguously, for H_3CONO and D_3CONO. A large rotamer shift, within the $\pi^* \leftarrow \pi$ electronic continuum (having maximum absorption intensity at 46400 cm^{-1}), and a small isotope effect, in the $\pi^* \leftarrow n$ bands above 25000 cm^{-1}, have been demonstrated.

The vibrational absorption spectra of methyl nitrite in the vapour phase show over-lapping of rotational envelopes, making identification difficult. Observation of a temperature effect on relative intensity becomes impossible in many cases. However, the temperature effects are readily observed in vibrations attributed to the –O–N=O group. Tarte[5] related the absorption intensity changes between 200 and 296 K to two sets of vibrational modes, one for each isomer. Thus, the 1681 cm^{-1} band of H_3CONO belongs to the thermally less stable rotamer but the 1625 cm^{-1} band to the more stable rotamer. Combining the i.r. and microwave data, all for the vapour phase, the 1625 cm^{-1} band can be assigned to the *s-cisoid* rotamer.

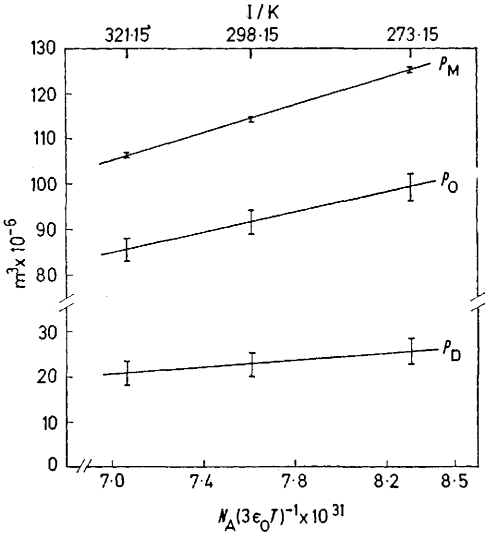

Figure. *Plots of total molar polarisation P_M, orientation polarisation P_O, and distortion polarisation P_D as a function of reciprocal temperature for mixtures of methyl nitrite rotamers in the vapour phase.*

We have investigated the photodecomposition[6] of H_3CONO or D_3CONO in argon matrices at mole fractions of 0·3—0·5%, using a liquid helium double Dewar, or Air Products Cryotip or Displex refrigerators as cooling devices, between 4 and 17 K. Because of efficient isolation under these conditions, the vibrational spectra consist of sharp lines, as measured on grating spectrometers. Photochemical behaviour was tested with either high- or low-pressure mercury lamps. Unlike the high-pressure lamp which emitted a broad range of effective radiation, the resonance lamp ($^3P_1 \rightarrow {}^1S_0$, 39413 cm^{-1}) reduced one series of sharp absorption lines (of either H_3CONO or D_3CONO) in intensity more rapidly than those of the other series, as H_2CO and HNO product absorptions appeared.† Thus,

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† In contrast, pyrolysis of methyl nitrite vapour in a flow reactor prior to freezing at 10 K yielded mainly H_3COH, H_2CO, NO, and H_3CO radicals.

the matrix absorptions at 806, 1040, 1422, 1444, and 1464 cm^{-1} belong to the same carrier as the 1663 cm^{-1} line and therefore to the *s-transoid* rotamer of H_3CONO, whereas other lines at 837, 985, 1406, 1436, and 1452 cm^{-1}, with 1611 cm^{-1}, belong to the *s-cisoid* rotamer. Likewise, matrix absorptions of D_3CONO at 550, 774, 1016, 1092, and 2252 cm^{-1} are related to the 1662 cm^{-1} line and thus to the *s-transoid* rotamer, unlike other lines at 595·5, 798, 1024, 1045, and 2275 cm^{-1}, with 1610·5 cm^{-1}, of the *s-cisoid* rotamer. This photochemical distinction indicates that the *s-cisoid* rotamer absorbs more strongly at 39413 cm^{-1} within the continuum, than does the *s-transoid* rotamer.

The preceding assignments for H_3CONO are mostly the reverse of those of Klaboe, Jones, and Lippincott[3] whose assignments were based on the interpretation by Gray and Pearson[6] of their relative permittivity measurements. Decrease of the effective dipole moment with increasing temperature seemed consistent[7] with the *s-transoid* rotamer being the more stable. These results[6] at only three temperatures, as shown in the Figure, yield a correlation coefficient of 0·9999 when treated by linear regression analysis. However, when the orientation polarisation P_0 values, calculated from the known dipole moments[4] and estimated mole fractions, are subtracted from the total molar polarisation P_M, the distortion polarisation P_D, composed of atomic (P_A) and electronic (P_E) contributions, may be obtained. That this value, $(23 \pm 3) \times 10^{-6}$ m^3 mol^{-1}, is much larger than the value of $13{\cdot}6 \times 10^{-6}$ m^3 mol^{-1}, which Gray and Pearson[7] estimated from bond refractions, demonstrates the unreliability of these additivity methods and the transfer of liquid phase data for applications with free molecules.

For alkyl nitrites (and HONO) in the ground electronic state and in the vapour phase, the N=O valence-stretching vibration *s-transoid* rotamers absorb above 1650 cm^{-1} and *s-cisoid* rotamers below 1641 cm^{-1}.

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