

## Rotational Isomerism in Nitrous Acid and Alkyl Nitrites

L. D'OR AND P. TARTE

Centre d'Analyse Spectral Moléculaire de l'Université de Liège,  
Liège, Belgium

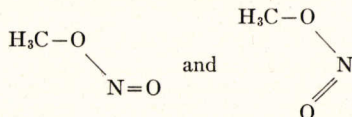
(Received May 28, 1951)

AT the present time, very little information is available on the vibrational spectra of alkyl nitrites. Kohlrausch<sup>1</sup> found (among numerous other lines) two strong Raman shifts, which are common to the nitrites studied: 1660 and 600  $\text{cm}^{-1}$ . Lenormant and Clément<sup>2</sup> published a few infrared data, which cover only the small region 5-8 $\mu$ .

We have taken the infrared spectra of a number of nitrites in the gaseous state between 2 and 23 $\mu$ . All the spectra exhibit a very strong absorption in the three regions 1660, 800, and 600  $\text{cm}^{-1}$ . These bands are attributed to the three fundamental frequencies of the O-N=O group (N=O stretching, N-O stretching, and O-N=O bending vibrations, respectively).

Much more important is the fact that all the nitrites studied show not one, but two, bands at 1650 and 600  $\text{cm}^{-1}$ ; moreover, the first nitrites (methyl, ethyl, propyl) exhibit also two bands at 800  $\text{cm}^{-1}$ ; and in the most simple one, namely, methyl nitrite, all the bands appear to be double.

An attractive explanation of these facts would be the existence of two forms of the nitrite molecule, such as



(rotational isomerism).

The temperature dependence of the intensity of the bands was studied in gaseous methyl nitrite. A temperature dependence was found for the following pairs of bands (which, in fact, represents all the bands between 6 and 15 $\mu$ ) (*i* represents an increase, *d* a decrease of the intensity of the band when the temperature is lowered):

1680 (*d*)-1625 (*i*); 1445 (*i*)-1375 (*d*); 1197 (*i*)-1131 (*d*);  
1045 (*d*)-993 (*i*); 844 (*i*)-814 (*d*).

The same temperature dependence has been found in a number of harmonic or combination bands between 3 and 6 $\mu$ .

Such a result supports strongly the hypothesis of rotational isomerism.

The nitrous acid itself HONO has been studied in the gaseous state, and the following pairs of bands have been observed (some of the frequencies reported here are not very accurate, owing to the overlapping of intense  $\text{N}_2\text{O}_3$  bands):

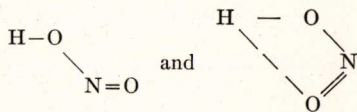
3590-3425, 1700-1640, 1370-1267, 855-793, 598-525  $\text{cm}^{-1}$ .

It is easy to recognize the 3 characteristic frequencies of alkyl nitrites (1700, 800, and 600  $\text{cm}^{-1}$ ), which once more appear to be double.

The remaining pairs (3590-3425 and 1370-1267  $\text{cm}^{-1}$ ) are undoubtedly the OH stretching and bending frequencies, because they are shifted at 2658-2537 and 1086-1015  $\text{cm}^{-1}$ , respectively, in the deuterated compound DONO.

The presence of two OH bands is not the result of intermolecular association because the nitrous acid has been studied in the gaseous state at low pressures (a few mm Hg); moreover, the relative intensity of the bands has been found to be independent of the pressure.

Consequently, intramolecular association seems to be the true explanation, and the two forms of the nitrous acid molecule can be written



Further experiments are in course and detailed results will be published in the near future.

We wish to thank the FNRS for financial support given us for this work.

<sup>1</sup> K. Kohlrausch and co-workers, *Monatsh.* **58**, 428 (1931); *ibid.* **61**, 397 (1932).

<sup>2</sup> H. Lenormant and P. Clément, *Bull. soc. chim. France*, 559 (1946).

