Some Remarks on the Spectra of Nitrites and Nitrosamines ⊘

P. Tarte

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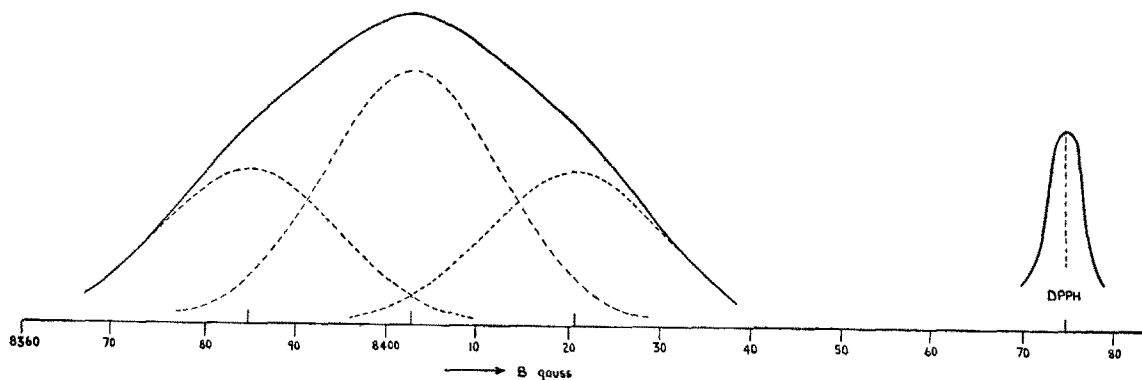
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FIG. 1.

of the F-nucleus of 2.6 mm would lead to a triplet splitting of 5.6 gauss. The existence of a g-shift of positive sign characteristic of halogen orbitals and the larger value of the triplet splitting would indicate that the extra electron participates to a certain extent in the CF bonding. Hyperfine interaction of the electron with more distant surrounding the F-nuclei would account for the large width (23 gauss) of the resonance lines.

1 E. E. Schneider and T. S. England, Physica 17, 221 (1951).
2 Schneider, Day, and Stein, Nature 168, 645 (1951).
3 E. E. Schneider, Trans. Faraday Soc. (to be published); see also Gordy, Smith, and Trambarulo, Microwave Spectroscopy (John Wiley and Sons, Inc., New York, 1953), p. 239.

Some Remarks on the Spectra of Nitrites and Nitrosamines

P. TARTE
University of Liège, Liège, Belgium
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IN a recent paper,[1] Haszeldine and Jander have reported and briefly discussed the ir and uv spectra of a series of nitroso-compounds. As we have worked for many years in this field, we should like to add some comments to their data and interpretations.

A. Alkyl nitrites.—(1) Haszeldine and Jander have compared the uv spectra of alkyl nitrites in light petroleum and ethanol. This method is not reliable since the mixing of a nitrite, R^1ONO, with an alcohol, R^2OH, is followed by a rather rapid reaction (which is limited to a chemical equilibrium): $R^1ONO + R^2OH \rightleftharpoons R^1OH + R^2ONO$. In the peculiar case studied here (butyl and amyl nitrites in ethanol), the error is not very serious because the uv spectra of ethyl, butyl, and amyl nitrites are very similar. But anyway, the observed spectrum is not the spectrum of a pure compound, and it is evident that another polar solvent should have been chosen.

(2) Rotational isomerism was first proposed by us in 1951[2] and fully confirmed as a general property of alkyl nitrites.[3] We should like to point out that our hypothesis of rotational isomerism is based, not merely upon a study of the doubling and temperature dependence of bands of methyl nitrite in the 6μ region (as it seems to appear from reference 1), but upon (a) a study of the doubling and temperature dependence of *all* the bands (between 3 and 15 μ) of methyl nitrite[3] and monodeuterated methyl nitrite,[4] (b) a systematic study of the uv and ir spectra of 15 alkyl nitrites[3] (rotational isomerism was deduced here from the doubling of the bands of the functional group $O-N=O$), and (c) a study of the nitrous acid (light and heavy) itself.[5]

B. Dialkylnitrosamines.—We agree with the statement that "The ir spectrum of dimethylnitrosamine dissolved in chloro-

form . . . is substantially identical with that of the liquid nitro-samine"; but the conclusion "Dimerisation . . . (analogous to C-nitrosodimers) . . . is thus improbable" may be considered as premature. We have studied the ir spectra of a series of dialkyl-nitrosamines in the liquid, dissolved (nonpolar solvent: CCl_4), and gaseous states[6] and, in the case of dimethylnitrosamine, our results are as follows: the band observed at 1317 cm^{-1} in the liquid is significantly weakened in solution and completely disap-pears in the gas; on the other hand, the band at 1448 cm^{-1} in the liquid is shifted to 1490 cm^{-1}, with a strong increase in intensity in the gas. Such spectral changes are characteristic of strong associations, and our interpretation is the following:

Liquid 1317 cm^{-1} $\nu_{N=O}$ frequency of associated molecules
     1448 cm^{-1} $\nu_{N=O}$ frequency of nonassociated molecules
Gas 1490 cm^{-1} $\nu_{N=O}$ frequency of free molecules

(For the discussion of these assignments, see Tarte.[6])

1 Haszeldine and Jander, J. Chem. Soc. 691 (1954).
2 D'Or and Tarte, J. Chem. Phys. 19, 1064 (1951).
3 P. Tarte, J. Chem. Phys. 20, 1570 (1952).
4 P. Tarte, Bull. Soc. Chim. Belges 62, 401 (1953).
5 P. Tarte, Bull. Soc. Chim. Belges 59, 365 (1950). D'Or and Tarte, Bull. Soc. Roy. Sci. e. Liège, 685, 478 (1951).
6 P. Tarte, Bull. Soc. Chim. Belges (to be published).

Further Remarks on the Spectra of Nitrites and Nitrosamines

R. N. HASZELDINE AND J. JANDER
University Chemical Laboratory, Pembroke Street, Cambridge, England, and Chemische Laboratorium der Universitat, Freiburg, Germany
(Received November 29, 1954)

(a) The well-known preparative method for methyl nitrite depends on the ready removal of methyl nitrite (b.p. $-14°$) from the equilibrium:

$$C_5H_{11}ONO + CH_3OH \rightleftharpoons C_5H_{11}OH + CH_3ONO.$$

Escape of any ethyl nitrite (b.p. 17°) produced by a similar equilibrium involving amyl nitrite and ethanol was prevented by deliberate choice of conditions (temperature 10–12°; sealed silica cells) for our measurements. Furthermore, since an independent method (to be published) shows that the amount of ethyl nitrite present at equilibrium is <10–20 percent, the spectrum recorded is in fact predominantly that of amyl nitrite in ethanol. Amyl and butyl nitrites in other solvents (e.g., dimethylformamide; ace-tonitrile), where equilibria of the above type cannot exist, have spectra identical with those in ethanol and light petroleum.

(b) Dr. Tarte's paper[1] on alkyl nitrites was acknowledged in our publication, but lest this was inadequate it should be made clear that the interpretation given of the infrared spectra of alkyl nitrites is based upon Tarte's original and prior postulate of rotational isomerism in these and similar compounds.

(c) Liquid dimethylnitrosamine shows four strong bands at 6.92, 7.10, 7.60, and 7.76 μ of approximately equal intensity [Fig. 1(a)]. The spectrum of a solution in chloroform [Fig. 1(b)] shows scarcely any change in the position and relative intensities of these bands, or in the band at 9.53 μ, and it was this which led to the conclusion that dimerisation to give $R_2N\cdot N(O^-)\cdot N^+$ (:O)NR_2 (analogous to C-nitroso-dimers), although it would explain the shift of the N:O vibration, was improbable, since partial dissociation with subsequent change in spectrum was to have been expected. The spectrum of a carbon tetrachloride solution was subsequently found to show appreciable change in several bands; however [Fig. 1(c)], the 6.92 μ band moves to
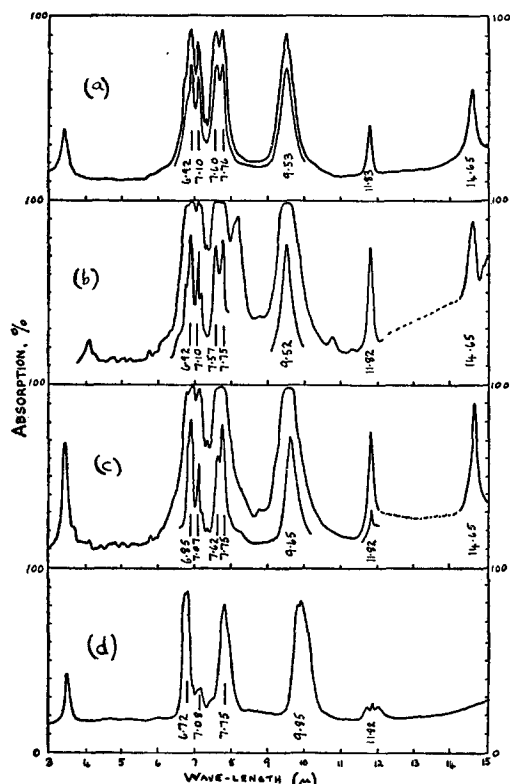

FIG. 1. Absorption spectra of dimethylnitrosamine. (a) Liquid capillary films. (b) Approximately 50 percent and 5 percent solutions in chloroform 0.025 mm cell. (c) Approximately 50 percent and 5 percent solutions in carbon tetrachloride 0.025 mm cell. (d) Vapor in 10 cm gas cell heated at 120°.

6.85 μ, but relative to the 7.76 μ band scarcely changes in intensity and the 7.10 and 7.60 μ bands move to 7.07 and 7.62 μ and are appreciably weakened relative to the 7.76 μ band. The 9.53 μ band shifts to 9.65 μ, but the 11.83 and 14.65 μ bands which appear in the pure liquid remain unchanged in both solutions. Finally the spectrum of dimethylnitrosamine vapor at 120° [Fig. 1(d)] shows the 7.60 μ band as only a weak shoulder, and the 7.1 μ band as a weak peak. The strong bands in the spectrum are now at 6.72, 7.75, and 9.85 μ. We assign the 6.72 μ band to the N:O bond in monomeric dimethylnitrosamine, and agree with the conclusion independently reached by Tarte, namely that in liquid dimethylnitrosamine hydrogen-bonding or association, as suggested earlier but rejected on the basis of the chloroform solution spectrum, must in fact be involved. A detailed discussion of the assignment of the 7.75, 7.07, and 7.62 μ bands, and of the solution and vapor spectra of other nitrosamines, is deferred to a paper to be submitted shortly to the *Journal of the Chemical Society*.

(d) We would take this opportunity of correcting a typographical error in our paper, which was carried through to other papers,[2] namely that the nitrogen-nitrogen vibration, assigned to the strong band in the 9.15–9.55 μ region for liquid nitrosamines, appeared in print as N—O instead of N—N.

[1] P. Tarte, J. Chem. Phys. **20**, 1570 (1952).
[2] R. N. Haszeldine and J. Jander, J. Chem. Soc. 697, 919 (1954).

## Pure Rotational Spectrum of H₂Se between 50 and 250 cm⁻¹

E. D. PALIK*
Department of Physics, The Ohio State University, Columbus, Ohio
(Received February 21, 1955)

SEVERAL vibration-rotation bands of H_2Se have been measured by Cameron, Sears, and Nielsen.[1] The fairly simple structure of the observed bands suggests that the molecule is an almost accidently symmetric rotator with the apex angle $2\alpha \approx 90°$ and $a \approx b \approx 2c$ where a, b, and c are the reciprocals of inertia.

The pure rotational spectrum of H_2Se has been observed in the spectral region between 50 and 250 cm⁻¹ using the far infrared spectrograph in this laboratory.[2] The gas was prepared by a method involving the chemical reaction

$$Al_2Se_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2Se.$$
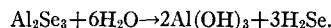
The gas, dried with P_2O_5, was introduced into a cell 7.5 in. long having polyethylene windows 0.01 in. thick. Several spectrograms were obtained using gas pressures between 3 and 12 cm Hg.

A portion of the observed spectrum is shown in Fig. 1. It consists of a series of strong lines with approximately constant spacing $2c$, with some weaker lines between these main lines. These strong lines are indicated by arrows. Taking into consideration the selection rules $J=0$, ± 1 and $++\leftrightarrow--$ and $+-\leftrightarrow-+$ for dipole moment along the axis of intermediate moment of inertia,[3] the strong series can be identified with transitions between low τ levels, for example $7_{-6}-6_{-6}$, $8_{-7}-7_{-7}$, $9_{-8}-8_{-8}$. Some of these transitions are indicated in Fig. 1. A weaker series of lines, marked by crosses in Fig. 1, is found to have approximately constant spacing $2a$. These are assigned to high τ transitions, for example 7_6-6_6, 8_7-7_7, 9_8-8_8. The spacing of the lines in these two series give approximate values for a and c, and b was obtained using the fact that $I_c = I_a + I_b$ for a planar figure. Making use of the approximate expression for the energy levels of a slightly asymmetric rotator

$$F(J,K)_{\text{oblate}} = \tfrac{1}{2}(a+b)J(J+1) + [c - \tfrac{1}{2}(a+b)]K^2$$

given by Herzberg,[4] it was possible to calculate the pure rotational spectrum. This approach leads to a tentative assignment of several of the other lines which also form series which are less evident than the two main series.

The analysis was refined by using the Cross, Hainer, King tables[5,6] to calculate energy levels and intensities. It was possible to assign most of the lines between 50 and 150 cm⁻¹. Many of the lines of higher frequency were assigned tentatively, but a quantitative centrifugal stretching correction has not been too successful
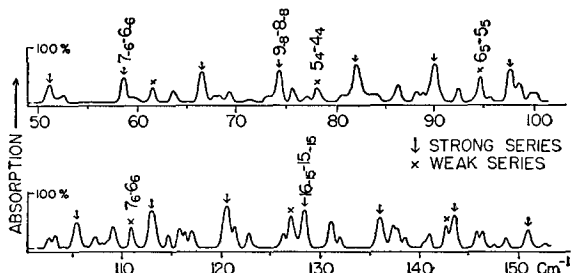

FIG. 1. Pure rotational spectrum of H₂Se.