

The InfraRed Absorption and Reflection Spectra of KHF2 and of KDF2

J. A. A. Ketelaar

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The Exchange Reaction between Gaseous and Combined Nitrogen

GEORGES G. JORIS

Frick Chemical Laboratory, Princeton University, Princeton, New Jersey
September 9, 1941

THE exchange reaction between gaseous and combined nitrogen recently reported in a letter to this journal by Yoshio Nishina, Takeo Iimori, Hideo Kubo and Hiromi Nakayama¹ has been reinvestigated using stable heavy nitrogen isotopes N^{30}_2 and N^{29}_2 . The composition of the initial gaseous mixture was $N^{28}_2 : N^{29}_2 : N^{30}_2$, 1000 : 204 : 100. Aqueous solutions of $NaNO_2$, $NaNO_3$ and $NH_2OH \cdot HCl$ at a concentration of 1/20 mole/l were used since they were reported to undergo the most rapid exchange between gaseous nitrogen and combined nitrogen.

No exchange was found as shown by the ratios N^{29}_2/N^{30}_2 with the shaking time indicated in Table I.

TABLE I.

SUBSTANCE TESTED	0 HOUR	6 HOURS	30 HOURS	360 HOURS
$NaNO_3$	2.04	2.05	2.05	2.04
$NaNO_2$	2.04	2.05	2.04	2.05
$NH_2OH \cdot HCl$	2.04	2.03	2.05	2.03

The results recorded with radioactive nitrogen must therefore be ascribed to difficulties arising in the technique of operation with the radioactive isotope. The present results are more reasonable, judged from the chemical standpoint and the stability of the ions containing nitrogen.

¹ Y. Nishina, T. Iimori, H. Kubo and H. Nakayama, J. Chem. Phys. 9, 571 (1941).

The Infra-Red Absorption and Reflection Spectra of KHF_2 and of KDF_2

J. A. A. KETELAAR

Laboratory for Inorganic and Physical Chemistry,
University, Leyden, The Netherlands
September 5, 1941

THESE compounds were investigated with a prism spectrometer in the quartz and rocksalt regions from 1–16 μ . When the investigation of ordinary potassium bifluoride was about finished a note came to my knowledge

from Messrs. Buswell, Maycock and Rodebush.¹ These authors only investigated the quartz region and here our results are in complete accordance. However my much more extensive investigations have led to conclusions essentially different from theirs.

The maxima at 1222 cm^{-1} and 1450 cm^{-1} (in reflection 1238, 1490 cm^{-1}) are both fundamental bands as indicated by the extreme strong absorption (> 90 percent for a layer of 8 μ) and by the high reflection percentages (55 percent and 60 percent, respectively) for both bands, thus excluding the explanation as a combination frequency for the latter band. The three other pairs of bands of decreasing intensity below 3500 cm^{-1} are due to combination frequencies of these fundamentals with 1, 2, and 3 times a frequency of 560–600 cm^{-1} . Of these pairs also the higher frequency component is the strongest band. The bands above this limit are due to the second harmonics² of the fundamentals at 3730 cm^{-1} (double) and at 5099 cm^{-1} , respectively, and

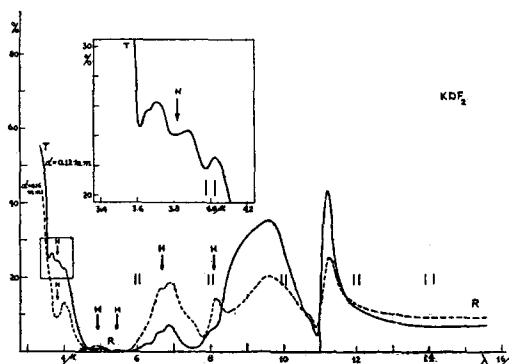


FIG. 1. Transmission and reflection curves for KHF_2 in the rocksalt region.

to their combinations with the same frequency of 560 cm^{-1} . The doubling of the band at 3730 cm^{-1} , also observed by the other authors, is due to a minor complication, the splitting of an higher harmonic due to higher terms in the potential function. The spectrum of KDF_2 is explained in just the same way with a shift of the fundamental bands by about $\frac{1}{2}\sqrt{2}$ to 891 cm^{-1} and 1046 cm^{-1} (in reflection). The inactive frequency at 560 cm^{-1} is found to be independent of the mass of the hydrogen atom. Thus a complete analysis of all bands in both spectra is possible with a single exception of minor importance.

The spectrum observed is due to the isolated HF_2 group as indicated by the identity between the spectra of KHF_2 and $RbHF_2$, save for a shift of a few cm^{-1} to lower values for the latter compound. Moreover specimens of KDF_2 containing 10 percent H give a mere superposition without any shift of the spectra of the pure compounds, thus proving the absence of any appreciable coupling between the groups. The fundamental double band is to be associated with the asymmetric valency oscillation of a linear three atomic model ("hydrogen frequency"), whereas the frequency at 560 cm^{-1} is the symmetric one ("fluorine fre-

quency"). The doubling of the active frequency can be shown to be only due to the existence of a double minimum in the potential curve for the hydrogen atom. A potential curve constructed according to the method of Dennison and Uhlenbeck³ from the experimental data gives 2570 cm^{-1} for the height of the potential hump with a separation of both levels of 25 cm^{-1} and 185 cm^{-1} for the ground and for the first excited level, respectively, the latter being already very near the top of the hill. The distance between both minima is found as only 0.70 angstrom units.

These results prove for the first time the existence of protonic resonance in the case of a hydrogen bond. On the other hand the small doubling of the ground level proves

definitely that even here this resonance does not contribute to any extent to the energy of the bond formation ($\frac{1}{2}h\nu = 0.04$ kcal./mole) which consequently must be considered to be entirely of electrostatic origin, due to the partial ionic character of the hydrogen atom. The structure of the HF_2 group is thus symmetric, resonating between F HF and FH F .

Experimental details are given in a forthcoming publication in the *Rec. trav. chim.*

¹ A. M. Buswell, R. L. Maycock and W. H. Rodebush, *J. Chem. Phys.* **8**, 362 (1940).

² The first harmonics are absent due to a selection rule valid for the crystal.

³ D. M. Dennison and G. E. Uhlenbeck, *Phys. Rev.* **41**, 313 (1932).