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Infrared experimental proof of the orientation of CH₄ adsorbed in NaA zeolite by means of the degeneracy splitting of the ν_3 band, in the temperature range 200-20 K

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Résumé. — Le spectre infrarouge du méthane adsorbé dans la zéolithe NaA évolue entre 200 et 20 K. La croissance de la bande interdite ν_1 et la levée de dégénérescence de la bande ν_3 témoignent de l'effet du champ électrique dans la cavité zéolithique. A partir de 80 K la molécule piégée dans son site d'adsorption s'oriente vraisemblablement en position tripode (C_{3v}) en face d'un cation Na^+ .

Abstract. — The infrared spectrum of methane adsorbed in NaA zeolite changes from 200 K to 20 K. The growth of the ν_1 forbidden band and the degeneracy splitting of ν_3 give evidence of the electric field in the zeolitic cavity. Below 80 K the molecule trapped in the adsorption site is probably oriented in a C_{3v} configuration in front of a Na^+ cation.

Synthetic NaA zeolites are porous solids presenting cavities of 11 Å mean diameter regularly distributed in the crystal lattice and connected by windows of 4 Å diameter [1]. The methane molecule adsorbed in these cavities is delocalized at room temperature, remains close to the surface at low temperature [2] and it is trapped at 80 K [3] (neutron scattering results). At the same time, the infrared analysis of adsorbed methane in the temperature range 300-200 K shows rotational wings on the ν_3 band and the forbidden ν_1 band induced by the electric field of the cavity [4].

In recent IR experiments, we have studied the same bands down to 20 K. The zeolite pellet is cooled in a He-cryostat; in the upper part of this cell, a furnace allows to dehydrate the zeolite at 670 K in 10^{-6} torr vacuum; the sample is lifted up and down by a mechanical device. The spectrometer is a Perkin Elmer 580 coupled to a computer. At each temperature, we have recorded separately the spectra of the cell with and without gaseous methane, and of the zeolite with and without adsorbed molecules. The spectrum of the adsorbed molecule is then obtained by subtracting the spectra of the gaseous phase and of the outgassed pellet. We have managed to adsorb ca. one molecule per cavity at each temperature (200, 180, 150, 100, 80, 50, 40, 20 K).

The experimental results show the following :

- The rotational wings on ν_3 decrease with temperature and the induced ν_1 band grows [4].
- From 100 K a splitting of ν_3 appears clearly. The two components very well defined below 80 K are 20 cm^{-1} apart : $\nu_3^1 = 3\,002\text{ cm}^{-1}$, $\nu_3^2 = 2\,982\text{ cm}^{-1}$.

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Fig. 1. — Infrared spectra of methane adsorbed in NaA zeolite at different temperatures. $\text{Log } I_0/I$ (arbitrary unit) = $f(\nu \text{ cm}^{-1})$.

The frequency of ν_1 is equal to 2882 cm^{-1} . The splitting of ν_3 shows a lowering in the molecular symmetry. It cannot be interpreted in terms of two different adsorption sites since it should give rise either to a double band for ν_1 or at least to a broadening of ν_1 . It is not the case as the widths of the bands decrease continuously with temperature.

By comparison of the spacing to the bandwidths at different temperatures, it is obvious that this splitting, if it exists above 100 K, cannot be seen when each component is too broad; indeed their full width at half maximum decreases from 14 cm^{-1} (100 K) to 5 cm^{-1} (20 K). This narrowing is evidently related to the trapping of the molecule in its adsorption site. We notice here that in neutron scattering experiments, the mass centre of CH_4 in NaA is seen at rest below 80 K. This site is probably in front of the Na_{III} cation (neutron diffraction [6]). In the equilibrium configuration of the couple $\text{CH}_4\text{-Na}^+$ found by potential energy calculations [7, 8] one threefold axis of CH_4 is oriented along the field of the cation with the three hydrogen plane facing Na^+ . As the electric field is of the order of 10^{10} V/m . The octupolar contribution is responsible of the orientation. There are four point sub-group of T_D (symmetry of the free molecule). The fact that ν_1 is now active and that ν_3 is split into two components instead of three allows us to conclude that the molecule is adsorbed in a C_{3v} configuration [5] with respect to the field.

A first analysis of the widths of these three bands shows that ν_1 and ν_3^1 evolve in a similar way while ν_3^2 is broader than ν_3^1 . This leads to assign the former to $\nu_3(a_1)$, vibration along the threefold axis (z axis of the C_{3v} molecule) oriented along the electric field.

Further experiments and analyses of the profiles and the intensities are now in progress. Indeed, the variation with temperature of the band profile, and hence the relaxation times of the dipolar moment correlation function, will give more information on the different rotational regimes.

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References

- [1] BRECK, D. W., *Zeolite Molecular Sieves* (Wiley and Sons) 1974.
 - [2] COHEN DE LARA, E., KAHN, R., *J. Physique* **42** (1981) 1029.
 - [3] COHEN DE LARA, E., KAHN, R., Proceedings of the 6th International Zeolite Conference, 1983.
 - [4] COHEN DE LARA, E., SELOUDOUX, R., *J. Chem. Soc. Farad. Trans. I* **79** (1983) 2271.
 - [5] HERZBERG, G., *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Co) 1968.
 - [6] KAHN, R., COHEN DE LARA, E., THOREL, P., GINOUX, J. L., *Zeolites* **2** (1982) 260.
 - [7] MOUCHE, E., COHEN DE LARA, E., KAHN, R. (submitted for publication, *Mol. Phys.*).
 - [8] SAUER, J., HOPZA, P., ZAHRADNIK, R., *J. Phys. Chem.* **84** (1980) 3318.
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