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Information on Chemical Kinetics from Rotational Spectroscopy

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Abstract – This article reports a short description of: (i) Reaction mechanisms unravelled by microwave spectroscopy (MW); (ii) Some kinetic processes taking place during a supersonic expansion; (iii) Unexpected chemical reactions proved in a microwave cavity.

Keywords: Microwave Spectroscopy; Reaction Mechanisms; Kinetic Processes; Chirality

Riassunto – Questo articolo riporta una breve descrizione di: (i) Meccanismi di reazione svelati attraverso spettroscopia a microonde (MW); (ii) Alcuni processi cinetici che hanno luogo durante un'espansione supersonica; (iii) Sorprendenti reazioni chimiche rilevate in una cavità a microonde.

Parole chiave: Spettroscopia Rotazionale; Meccanismi di Reazione; Processi Cinetici; Chiralità

A few years ago, we published an article entitled "Detection and characterization of impurities in commercial products with Fourier transform microwave spectroscopy": the rotational signatures of methyl pyruvate as an impurity were accidentally found and its rotational spectrum was assigned while recording the microwave spectrum of a 98% Sigma-Aldrich sample of methyl (S)-(-)-lactate [1, 2]. In [1], in the field of analytical chemistry, we outlined that, as to the application of MW in analytical chemistry, probably the most important success is related to the identification of signals reaching the earth from interstellar space. It has been possible, indeed, to observe with this technique more than 200 molecular species from remote sources in space [3].

Still in the same article, we mentioned that already in 1981 the MW technique was used to discriminate between different deuterated products while studying the steric course of the reaction of ethylene oxide with hydrogen halides in the gas phase [4]. The author of the present article made the MW measurements, but his contribution was acknowledged with a misspelled name (Carminati instead of Caminati). The MW measurements, made in a conventional absorption cell, were essential in the determination of which product was formed because



the two isotopologues of D_2 -ethylene oxide (see Fig. 1) have completely different rotational spectra.

Fig. 1. The two isotopologues of $\mathrm{D_2}\text{-}\mathrm{ethylene}$ oxide have completely different rotational spectra.

Now we take into account the main kinetic effects associated with a supersonic expansion typical of cavity Fourier transform spectroscopy: (i) Appreciable populations of only low energy rotational states (more or less according to the Boltzmann equation); (ii) Appreciable populations of only low energy vibrational states but depending on the vibrational spacings, "propensity rules" and carrier gas; (iii) Isotopic effects and formation of chiral adducts; (iv) Conformational relaxations, that is high energy conformers can relax to more stable conformers if there is a low energy path, also depending on the mass of the carrier gas.

Regarding point (ii), we described the vibrational relaxation in pyridine upon supersonic expansion [5], measuring the rotational spectra of five vibrational states by millimeter wave absorption spectroscopy in a supersonic expansion. We found that the intensities of the lines of the vibrational satellites with respect to the ground state after the supersonic expansion depend on the kind of carrier gas, backing pressure, pyridine concentration, and symmetry of the rotational and vibrational states. The overall behavior is represented in Fig. 2.

As to point (iii), isotopic effects, they are related to the different vibrational energies for bonds involving different isotopes. These effects are remarkable for the H/D pair, as shown in Fig. 3, since the mass ratio is about 1/2.



Fig. 2. Ratios between the jet experimental and calculated values of the intensity ratios $I(v_i=1)/I(v=0)$ quantities. *i* runs over the vibrational modes. The calculated values are obtained with Boltzmann equation relative to the starting temperature (298 K). The upper lines reports the quantum numbers of three rotational transitions with different symmetries of the involved rotational levels.



Fig. 3. Qualitative description of the origin of the isotopic effects, especially pronounced for the $H \rightarrow D$ isotopic substitution.

For this reason, when HDO acts a proton donor in a hydrogen bonded adduct, the isotopologue HOD…X (X is a proton acceptor) is much more stable than the DOH…X one. For example, in the case of the adduct ethylene oxide (EO)-water, the supersonic expansion rotational spectrum of the HOD…EO species was three times more intense than that of the DOH…EO isotopologue [6]. The understanding of this feature can be very important for the observation of hydrogen bonded complexes in low temperature-low pressure conditions, as, for example, in interstellar space, where the D/H ratio can be much larger than on earth. The isotopic effect are remarkable, however, also for heavier atoms. For example, for the isotopic pair 20 Ne/ 22 Ne in the rotational spectrum of [1,1]-Pyridine-Ne₂ [7]. The shape of the molecular adduct is shown in Fig. 4a.

The isotopic abundances of ²⁰Ne and ²²Ne are 90.5 and 9.2 %, respectively. However, as shown in Fig. 4b, it turns out that in the jet conditions the ground-state populations of the Pyridine-²⁰Ne²²Ne and Pyridine-²²Ne²²Ne isotopologues increase by factors up to \approx 20 with respect to that of the parent (Pyridine-²⁰Ne²⁰Ne) species. The mass increase for the heavier isotopomers results in a lower zero-point energy level and larger dissociation energy. Then, the isotopic enrichment can be explained by the thermal quasi-equilibrium reached as a result of repeated dissociation and re-formation of the trimers in the lowtemperature molecular expansion [8].

This kind of unexpected enrichments of slightly more stable isotopologues led us to suppose that the formation of chiral complexes within a supersonic could lead to a higher concentration of the most stable form originated from parity violation [9]. For example, the trimer of trifluoromethane has, according to the rotational spectrum [10], a chiral structure (see Fig. 5).

The two mirror images can interconvert by a set of rotations and breaking/reformation of several weak hydrogen bonds. If one of the two enantiomers is slightly more stable, the formation and reformation processes which take place in the nozzle throat would favorite this form.



Fig. 4. (a) Shape of [1,1]-Pyridine-Ne₂. (b) Recorded 4_{14} - 3_{03} transitions of three isotopologues of the complex (¹⁵N)pyridine with 2 Ne atoms. The intensities of the ²²Ne species are unusually high.



Fig. 5. Chiral shape of the trimer of difluoromethane.

In principle, a plausible zero enantiomeric excess could be observed with the "enantiomeric-specific MW detection" [11-13]. This could suggest the possibility of observing the effects of parity violation (ΔE_{pv}).

Concerning point (iv), conformational relaxation, it is well known that high energy conformers can relax to low energy conformers (generally to the global energy minimum), when the barrier to conformational conversion is lower than 2kT [14]. However, the pathways and the atomic weight of the carrier gas play important roles. For example, in the case of the tetrahydropyran...HF complex, both equatorial and axial rotamers are observed when using He as carrier, but only the most stable equatorial form has been detected when using Ar [15]. As to unexpected reactions, many molecular adducts of formic acid with various (mainly organic) molecules have been studied by MW [16], most of them in Bologna, see Fig. 6.

However, when we tried to assign the rotational spectra of adducts of formic acid with simple acids, we did not succeed. Vice versa, we could assign 1:1 molecular adducts of formic acid with tertiary alcohols.

Why primary and secondary alcohols led to esterification when mixed with formic acid and subject to super-



Fig. 6. Formic acid forms easily molecular adducts with most molecules, but not with primary or secondary alcohols.



[a] One transition example is given for each of them. All spectra cover a range of 0.4 MHz. The central frequency (ν_c) and the number of accumulation cycles (N_c) of each spectrum are given.

Fig. 7 Details of the spectra of the esters formed in a supersonic expansion of binary mixtures of carboxylic acids with primary and secondary alcohols, and adducts formed with tertiary alcohols.



Fig. 8. Energy profiles of the multiple chemical process paths for the FA-methanol, FA-ethanol, FA-isopropanol, and FA-tert-butanol mixtures. The observed species are indicated with a rectangular frame.

sonic expansion, while tertiary alcohols do not? An explanation attempt is given in our article "The Borderline between Reactivity and Pre-reactivity of Binary Mixtures of Gaseous Carboxylic Acids and Alcohols" [17]. There we took into account the investigation of carboxylic acids with five primary or secondary alcohols, which lead to esterification, and with two tertiary alcohols, which brought to the formation of the molecular adduct (see Fig. 7).

We tried to interpret the different behavior of tertiary alcohols with chemical dynamics calculations (see Ref. [17] for the details). The results are shown in Fig. 8.

It seems that the ΔG values are the most significant ones in interpreting the experimental evidence. Their changes (ΔG^0) in going from the adducts to the ester are close to zero for the tertiary alcohols, but about -3 to -5 kcalmol⁻¹ for the primary and secondary alcohols.

We believe that the presented results can be useful to understand some aspects of astrochemical kinetics.

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