Organic Matter in Space
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Molecular spectral line surveys and the organic molecules in the interstellar molecular clouds

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Abstract. It is known that more than 140 interstellar and circumstellar molecules have so far been detected, mainly by means of the radio astronomy observations. Many organic molecules are also detected, including alcohols, ketons, ethers, aldehydes, and others, that are distributed from dark clouds and hot cores in the giant molecular clouds. It is believed that most of the organic molecules in space are synthesized through the grain surface reactions, and are evaporated from the grain surface when they are heated up by the UV radiation from adjacent stars.

On the other hand the recent claim on the detection of glycine have raised an important issue how difficult it is to confirm secure detection of weak spectra from less abundant organic molecules in the interstellar molecular cloud.

I will review recent survey observations of organic molecules in the interstellar molecular clouds, including independent observations of glycine by the 45 m radio telescope in Japan, and will discuss the procedure to securely identify weak spectral lines from organic molecules and the importance of laboratory measurement of organic species.

Keywords. ISM: molecules, line: identification, molecular data

1. Introduction

In recent years highly sensitive observations on interstellar molecules have been conducted by, e. g., the Greenbank Telescope (GBT) and the Nobeyama 45 m telescope. Such observations provided lots of new insights on new species, molecular abundances, exsistence of organic species in a wide variety of objects, and so on. These will be the basis in understanding the interstellar chemistry.

Remarkable progress was made in observing large, complex organic species, e. g., glycolaldehyde, the simplest sugar, (Hollis *et al.* 2000) or glycine, the simplest α-amino acid, (Kuan *et al.* 2003), which may link to the understaning to the origin of life in the universe. However some observed spectra have weak signal intensities and these spectra are contaninated by other spectra, leading the debates that such observation results are plausible or not.

In this paper I will review several observations on organic molecules toward cold and dark clouds and star forming regions, and will discuss what are needed to verify a new identification in this era of crowded spectra.

2. Molecular Line Survey toward TMC-1

Cold dark interstellar clouds have been extensively studied as the formation sites of low-mass stars and planetary systems since their identification to the interstellar molecular

clouds in 1970's. A variety of exotic chemical compounds found in molecular clouds, especially those containing carbon atoms, attracted strong interests in connection with the formation of planets and the origin of life in the universe. Recent radio and IR observations towards comets collected important evidence that comets, 4.6 billion year-old fossil bodies of the proto-solar-system nebula, keep molecular composition similar to that in cold dark clouds. Therefore, the chemical evolution in cold dark clouds is basically important as the initial process of interstellar matter evolution toward the planets, and, ultimately to life.

Chemical reactions in dark clouds are not yet fully understood, and many unknown molecules might be synthesized in dark clouds. It is essential for understanding the chemical reactions in dark clouds, therefore, to make an unbiased frequency survey that can detect all molecular lines, including unpredicted lines of unknown molecules.

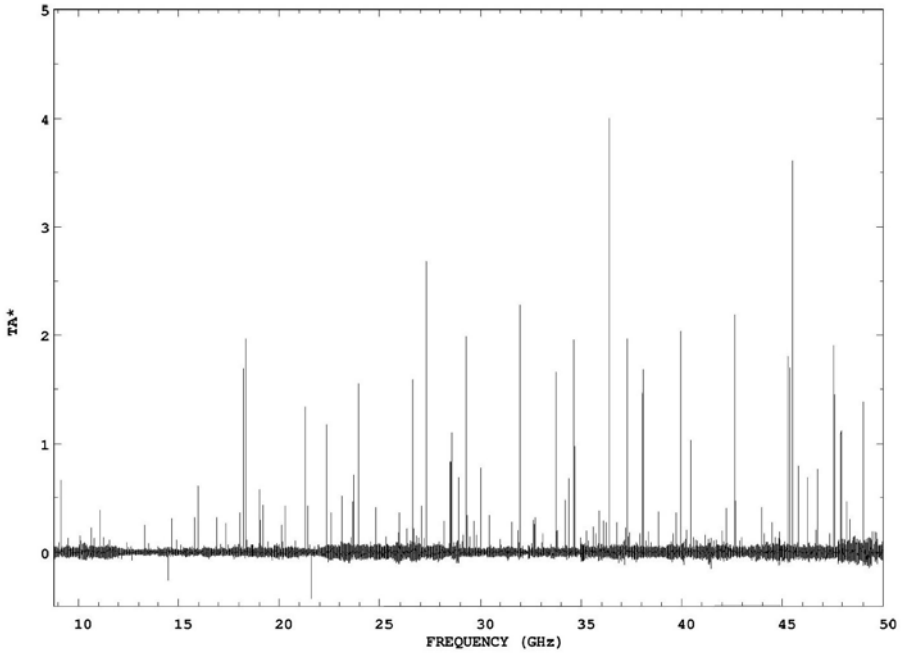

Figure 1. A compressed atlas of the 8.8–50 GHz spectrum toward TMC-1 (cyanopolyyne peak).

Kaifu *et al.* (2004) published a molecular spectral line survey data toward a dark cloud, the cyanoplyyne peak of TMC-1, in the frequency range between 8.8 and 50 GHz (see Figure 1), using the 45-m mm-wave telescope of the Nobeyama Radio Observatory†. They detected 414 lines from 38 molecules. Most of the molecules are linear carbon chain species and their derivatives, and there are only a few organic species such as CH_3OH, CH_3CHO, HCCCHO and CH_2CHCN. More saturated species, e. g., C_2H_5CN and $HCOOCH_3$, were not detected at all. According to their preliminary analysis (Ohishi & Kaifu 1998), these species generally have less abundances than major linear carbon chain molecules such as HC_3N and CCS, and it would be possible to conclude that the organic species are not the main constituent in the cold and dark clouds.

† Nobeyama Radio Observatory is an open-use facility for mm-wave astronomy, being operated under the National Astronomical Observatory of Japan (NAOJ).

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3. Detection of Organic Species in the Early Stage of Protostellar Evolution

So far large organic molecules (e.g., $HCOOCH_3$, $(CH_3)_2O$, and C_2H_5CN) were observed with high abundances toward the hot cores such as Orion KL, Sgr B2(N) and W51 e1/e2 where O/B stars are formed. Such highly saturated molecules are difficult to be produced by gas-phase chemical reactions under low-temperature conditions, and hence the grain surface chemistry is thought to play an important role in their production. When star formation takes place, the grain mantles are heated up by various activities of newly born stars, supplying parent molecules, like CH_3OH and H_2CO, into the gas phase through evaporation processes. Subsequent gas-phase reactions under high-temperature and high-density conditions would produce large organic molecules.

Recently detections of large organic species were reported toward the hot corinos in IRAS 16293-2422 (Cazaux *et al.* 2003, Bottinelli *et al.* 2004, Kuan *et al.* 2004). Further detection of $HCOOCH_3$ toward NGC1333 IRAS4B (Sakai *et al.* 2006) and NGC2264 MMS3 (Sakai *et al.* 2007) were reported. Figure 2 shows the spectrum of $HCOOCH_3$ toward NGC1333 IRAS4B that is a class 0 low-mass protostar with an estimated age of a few 100 years. This suggests that the complex organic molecules appear from the very early stage of protostellar evolution.

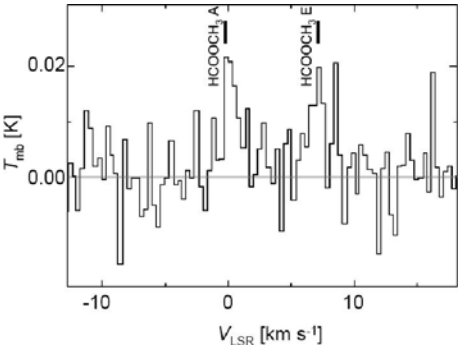

Figure 2. A Spectrum of $HCOOCH_3$ toward NGC1333 IRAS4B taken by the Nobeyama 45 m Telescope.

Sakai *et al.* (2007) found the $HCOOCH_3$ distribution, reveald by the Nobeyama Millimeter Array, seems to be similar to the case of Orion KL Compact Ridge where the molecular peak is shifted from the dust continuum peak, and suggests that such distribution similarity would give a hint to understand the formation of $HCOOCH_3$ in hot corinos and hot cores.

Since other highly saturated organic species, such as C_2H_5OH, $(CH_3)_2O$ and C_2H_5CN, are observed in hot cores, it would be necessary to conduct deep observations on these species toward low-mass protostars to further understand the formation mechanism and evaporation conditions of organic species.

4. Recent Reports of Large Organic Species toward High Mass Star Forming Regions

In the last several years many very large organic molecules were reported to be detected. This is primarily because of the powerful observation performance of the Greenbank Telescope (GBT) together with improvement of the receiver sensitivities.

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These molecules include glycolaldehyde (CH_2OHCHO) (Hollis *et al.* 2000), ethyleneglycol ($(CH_2OH)_2$) (Hollis *et al.* 2002), glycine (NH_2CH_2COOH) (Kuan *et al.* 2003), propenal (CH_2CHCHO) and propanal (CH_3CH_2CHO) (Hollis *et al.* 2004a), acetone ($(CH_3)_2CO$) (Friedel *et al.* 2005), cyanoallene (CH_2CCHCN) (Lovas *et al.* 2006), acetamide (CH_3CONH_2) (Hollis *et al.* 2006), and cyanoformaldehyde (CNCHO) (Remijan *et al.* 2008).

The report on the detection of glycolaldehyde (Hollis *et al.* 2000) toward Sgr B2(N) by the Kitt peak 12 m telescope was an epoch making one, because glycolaldehyde is the simplest sugar and really a prebiotic molecule. However the reported spectra had low signal to noise ratios, and some of them appeared on the shoulders of other molecular lines. Such a situation had led to dabates if the detection was secure. In 2004 Hollis *et al.* (2004b) made observations of glycolaldehyde by the GBT in four frequency ranges below 22 GHz, showing data with sufficient signal to noise ratios. Three transitions out of four showed absorption features at 63 kms^{-1} where absorption features from other already known species appear. The GBT observations made the detection of glycolaldehyde secure.

On the other hand the cases for propenal and ethyleneglycol are different. Only two propenal lines were reported toward Sgr B2(N), and the absorption features at 63 kms^{-1} is apparent for only one line. Five ethyleneglycol data were reported, however, they appeared on the shoulders of other molecular lines. This situation made difficult to investigate if the intensity distribution was reasonable for species observed toward Sgr B2(N). Therefore it may be concluded that the detection of propenal and ethyleneglycol have not yet been confirmed.

The report on the detection of glycine, the simplest α-amino acid, by Kuan *et al.* (2003) had the similar situation in that the signal to noise ratios were not so high and many spectra seemed to be contaminated. They observed 27 frequency bands of glycine conformer I toward Orion KL, Sgr B2(N) and W51 e1/e2, however, only three of them were reported to be observed from three objects. Intensity analyses by means of the rotation diagram were made, and the distributions seemed plausible. However, the derived column densities of glycine for three sources had similar values, inconsistent with a fact that in most cases a column density of a molecule toward Sgr B2(N) is higher by about two order of magnitudes than those toward Orion KL and W51 e1/e2.

Therefore we made an independent observations by the 45 m telescope at Nobeyama. Because the glycine spectra had high possibility of contamination, we carefully examined our past observed data to find "clean spectrum windows" where no transitions from other known abundant species exist.

Figure 3 shows a spectrum observed toward Orion KL at around 90 GHz. There are transitions of glycine conformer I at 90043.13 MHz ($15_{1,15}$–$14_{1,14}$, upper energy = 24.63 cm^{-1}), 90049.71 MHz ($15_{0,15}$–$14_{0,14}$, upper energy = 24.62 cm^{-1}), and 90056.98 MHz ($15_{1,15}$–$14_{0,14}$, upper energy = 24.63 cm^{-1}). The expected brightness temperatures for these transitions are around 20 mK when we used the column density and the roration temperature derived by Kuan *et al.* (2003). One peak coincides with the glycine transition at 90043.13 MHz with around the expected intensity, however, other two are not clearly seen. The line at 90043.13 MHz was not identified when we investigated available molecular line databases, leaving a possibility that the line could be identified to the glycine line. However we noticed that there is another line next to the 90043.13 MHz line with a similar line intensity. Such a "doublet line" could be due to the internal rotation, and it is well known that the molecular abundance of $HCOOCH_3$ toward Orion KL is so high. We contacted a laboratory molecular spectroscopist, Dr. Hitoshi Odashima at

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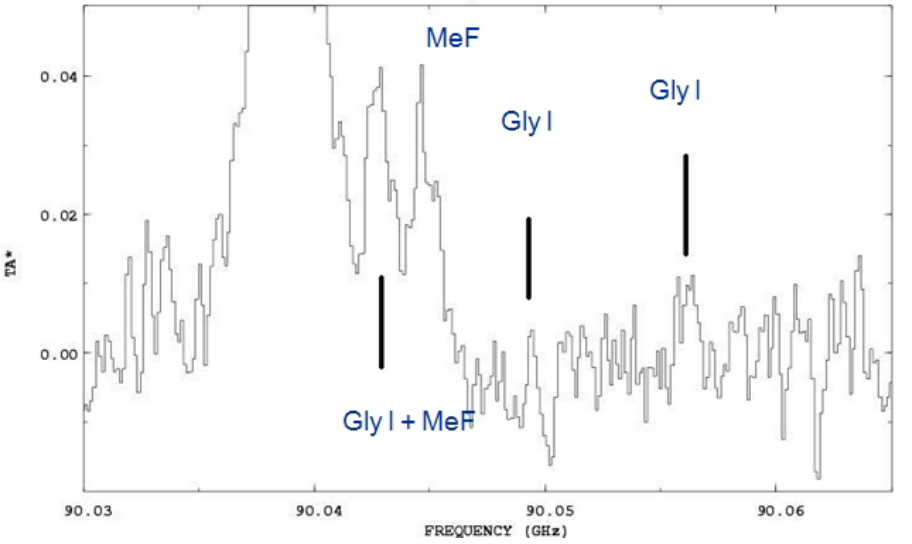

Figure 3. A Spectrum toward Orion KL at around 90 GHz where the Glycine (conformer I) transitions exist, that are shown by the vertical lines. MeF stands for $HCOOCH_3$.

Toyama University, Japan, asking if he had maesured weak lines of $HCOOCH_3$, and it was revealed that two unassigned lines of $HCOOCH_3$ matched the two lines above.

Therefore it can be concluded that the detection of interstellar glycine has not yet confirmed.

5. Toward Secure Line Identification

It was found that some reports on detection of a new interstellar molecule have not yet been confirmed.

Then what should we take into account toward secure line identifications?

Several issues may be listed toward secure line identifications, although not complete, as follows:

- Refer to reliable frequency data
- Many lines as possible, in "clean windows", with a consistent intensity distribution
- Expected lines should be observed with expected intensity
- Radial velocities should be consistent among observed transitions
- Observations in other sources with similar physical conditions (e.g. Orion KL, W51e1/e2) to see similar lines
- Less broad lines are desirable (e.g. NGC6334)

In the following subsections, I will disucuss some issues above.

5.1. *Reference to reliable frequency data*

It is crucial to refer to reliable frequency catalog data in order to make secure identifications.

There are several molecular line catalogs, such as the Cologne Database for Molecular Spectroscopy (CDMS) (Müller *et al.* 2001, Müller *et al.* 2005, http://www.ph1.uni-koeln.de/vorhersagen/), JPL Catalog (http://spec.jpl.nasa.gov/ftp/pub/catalog/catform.htm). These catalogues were compiled and maintained by microwave spectroscopisits, and the transition frequencies were calculated based on laboratory measurements. Most

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of the catalong data are highly reliable. However, it should be noted that some laboratory measurements were made long time ago and might have larger errors, resulting in larger uncertainties on the molecular constants. Since calculated transition frequencies are, roughly speaking, proportional to $J(J+1)$ where J is the rotational quantum number, high-J transitions may have much larger uncertainties in frequencies.

The laboratory reference papers should be visited, but it would be hard for many astronomers to judge if the laboratory measurements were reliable or not. It is suggested to contact to the catalogue maintenance persons who can be reached from the web pages above in cases when candidate lines toward new identifications show peculiar behaviors such as shifted radial velocities from well established values for the observed source, and so on. Such interdisciplinary communications would be so beneficial not only for astonomers but to molecular spectroscopits, because a laboratory measurement in a wide frequency range, that may be used for astronomical observations, is so time-consuming, and because it would be hard for spectroscopists without the support by, e. g., astronomers to get a new research fund to conduct such useful measurements.

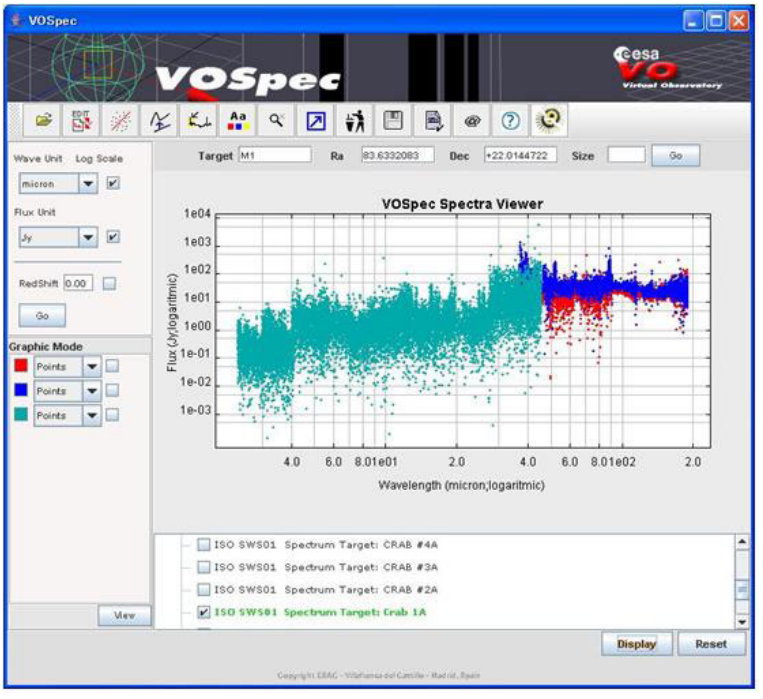

Figure 4. A snapshot of VOSpec that has a link to the atomic and molecular line catalogues.

Very recently a convenient tool, VOSpec (http://esavo.esa.int/vospec/), has been available. Figure 4 shows a snap shot of the VOSpec. This tool has been developed by the Eeuropean Space Agency Virtual Observatory (ESA-VO) team, and is a spectrum viewer that can access to registered spectral catalogs via Simple Line Access Protocol (SLAP) that has been standardized in the International Virtual Observatory Alliance (http://www.ivoa.net/). The ESA-VO team made experiments to connect CDMS and ESA-VO successfully. Therefore, it will be possible to access the CDMS and/or JPL catalogues via VO-compatible tools in near future.

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5.2. *Many lines as possible, in "clean windows", with a consistent intensity distribution*

Large organic species usually have large momenta of inertia, $I_{\rm A}$, $I_{\rm B}$ and $I_{\rm C}$, along the *a*-, *b*- and *c*-axis of the molecule, respectively. This means the rotational constants, $A \propto \frac{1}{I_{\rm A}}$, $B \propto \frac{1}{I_{\rm B}}$, and $C \propto \frac{1}{I_{\rm C}}$, will have smaller values. Then the rotational partition function, $Q \propto \sqrt{\frac{1}{ABC}}$, will have larger value. Assuming the Boltzmann distribution, the level population is proportional to $\frac{1}{Q}$, and the level population will be smaller, leading weaker intensities of transitions. Therefore it is another crucial point to find "clean windows" in spectrum as possible to avoid contanimation by other molecular transitions. "Clean windows" could be found by investigating published molecular spectral line survey data toward several sources and molecular line databases mentioned above.

Because large organic species tend to have weaker signal intensities, it is desirable to observe many (more than 5–10) non-contaminated lines as possible to find consistent intensity distribution and radial velocities. The rotation diagram method is often used to derive rotational temperature and column density of a molecule, because it is easy to use under the assumption that all line is optically thin. However it is known that the rotation diagram method may lead to wrong analysis result for the identification of interstellar molecules without the support of correct spectroscopic assignments for candidate lines (Snyder *et al.* 2005). A possible alternative method would be to use a non-linear least squares fitting method (Ohishi & Kaifu 1998).

6. Summary

Recent high-sensitivity observations toward the interstellar molecular clouds have revealed the following new insights, as follows:

- Fundamental molecular abundance toward TMC-1
- Organic molecules *n* several new compact sources
- Several new large organic molecules detected by the GBT and other telescopes

However, it was found that the interstellar glycine has not been confirmed yet, and the next generation radio telescopes, such as the ALMA, would give a clue to search for life-related species. In any case, careful observations with various point of view would be needed toward secure line identifications. And collaboration with spectroscopists would be crucial to have accurate and precise frequency data.

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Discussion

Ziurys: It is a very big problem because basically it is wall-to-wall lines when you get down to more sensitive limits. What people really need to do is to have an energy level diagram and just go through and make sure all the transitions below a certain energy and above a certain line intensity are there. This requires probably observations of multiple bands. Otherwise, it's so easy to make a mistake. I think we are just beginning to realize that it's so treacherous.

Ohishi: I agree with that. I wouldn't say more.

Ziurys: So I guess my comment is be careful on Sgr B2 and Orion and do lots of observations if you want to detect these things.

Matthews: Thank you for your elegant non-detection of glycine. It is possible that amino acids will never be seen as free molecules in space, but that doesn't rule out that space maybe swarming with potential amino acids in the form of large molecules like HCN polymers, which will give rise to many amino acids once it gets hydrolyzed. They are very stable in space and we can receive them later from comets, meteorite, etc. So even if one makes the statement that there are no free amino acids in space, it has really very little to do with the whole origin of life question because space may be swarming with amino acid because like hydrogen cyanide polymers.

Ohishi: I use millimeter-wave observations and glycine is below our detection limit, but many people say if we go to the sub-millimeter wave region with very high spatial resolution, we can look for glycine in very dense regions. There remain a possibility that amino acids can be detected in the gas phase in the near future, e. g., with ALMA.

Irvine: And of course we know there are lots of amino acids in meteorites.

Mumma: I notice in the spectrum you show that there were four transitions which were marked to have these proper frequencies and this was regarded as a definition of the molecules being correctly identified. The problem that I saw on that slide was one that at least one of the lines is in absorption, the others were in emission. I want to point out

that the issue of intensity is extremely critical, and particularly when radiative transfer is not being considered.

OHISHI: Yes, Sgr B2 is a very difficult source to understand. People say that there is hot area surrounded by cold cloud so the radiative transfer calculation needed to understand the intensity distribution correctly is very, very difficult.

MUMMA: so the question is how can one say that this is a detection unless you also explain the unusual intensity distribution?

OHISHI: We may need more high signal-to-noise ratio observations in different transitions, or we may need to observe other sources.

IRVINE: And also on what energy levels correspond to absorption and what energy levels correspond to emission.

The University of Hong Kong.

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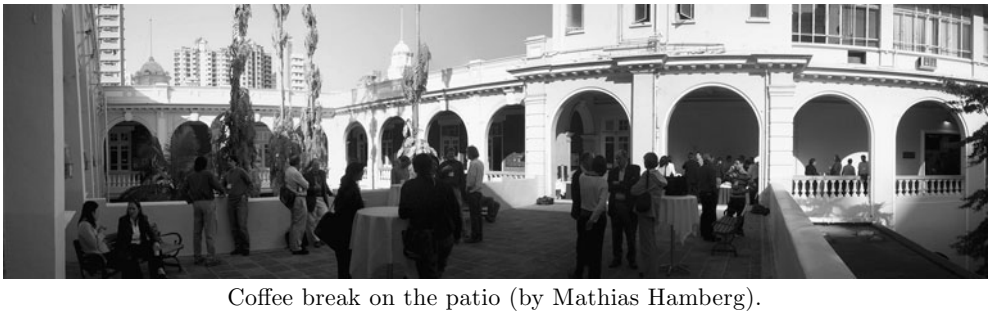
The delegates were welcomed by a traditional lion dance (photo by Dale Cruikshank).



Coffee break on the patio (by Mathias Hamberg).

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