

Infrared Spectroscopy and the Atmosphere

Measurements from space enable accurate monitoring of molecular abundances

Jean-Marie Flaud

In recent years, numerous studies concerning the atmospheric system have been published. However, we are still far from understanding the complex interplay of atmospheric dynamics and anthropogenous emissions. A key element in investigating the evolution of trace constituents in the troposphere and stratosphere is a global monitoring of the relevant molecules. This task is accomplished by state of the art instrumentation on satellites. This task is accomplished by state of the art instrumentation on satellites. The analysis of the corresponding atmospheric spectra requires the combination in the laboratory of the best experimental techniques and sophisticated models: we can now for example determine accurate line intensities for unstable molecules and model the spectrum of heavy species.

Molecular spectroscopy, besides its own interest as a scientific discipline, is a powerful tool used in a number of fields such as atmospheric physics, astrophysics, atmospheres of the planets, and combustion diagnostics. It allows one indeed to measure in a non-intrusive way numerous properties of the various media such as temperature, pressure and concentrations of constituents. As far as atmospheric physics is concerned, the past years have seen a noticeable increase of studies whose goals are a better understanding of the different phenomena driving the atmospheric system as well as the prediction of its evolution in the future. In particular human activities, important since the beginning of the industrial revolution, are strongly changing the atmospheric composition. One can quote, for example, the green house effect due to the emission of gases such as carbon dioxide or methane, or the decrease of ozone in the stratosphere clearly observed over the poles (ozone hole), or even pollution for which overarching issues such as air quality, free tropospheric ozone levels, acidic deposition, natural versus anthropogenic emissions are still open. These questions are tackled both from the theoretical point of view by developing chemical transport models (CTM) with the intention of simulating the distribution and evolution of trace constituents in the troposphere and stratosphere and from the experimental point of view using various platforms (ground networks, balloons, planes, satellites) and different techniques.



Fig. 1: View of the ENVISAT satellite. Among the experiments MIPAS and GOMOS are dedicated to the study of the terrestrial atmosphere. (Courtesy of M. Endemann, ESA)

Among them optical remote sensing methods are widely used. In particular, measurements from space are the only ones able to provide a continental or global view of the atmosphere. This is why a number of satellite experiments using various optical techniques (e. g., Radiometers, grating spectrometers, Fourier transform interferometers) have been launched. In the near future high quality optical remote sensing instruments working in the middle and thermal infrared such as MIPAS (Michelson Interferometer for Passive Atmospheric Sounding), TES (Tropospheric Emission Spectrometer), and others will be in operation. In all cases the analysis of the measurements requires the best possible knowledge of the spectral parameters (line positions, intensities, widths, absorption cross sections etc.) of the measured species and of their variations with temperatures and pressures. This is particularly true for the recent instruments which cover wide spectral ranges at rather high spectral resolutions with excellent signal to noise ratios. The spectral parameters are derived from experimental and theoretical spectroscopy, and, since obviously the accuracy of the retrieved profiles correlates with the quality of the spectroscopic parameters, given the improved capabilities (higher spectral resolution, better signal to noise ratio,...) of the new instruments, it is clear that new laboratory studies using the best experimental techniques

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and sophisticated theoretical models are required.

In many cases one has to face the „classical“ problem of laboratory work, i. e. reaching the required accuracy and determining it properly. This is an extremely difficult problem in itself, but in a number of cases one has to tackle even more challenging questions. Let us cite in particular the difficulty of measuring and generating accurate line intensities for unstable molecules or of modelling the spectrum of heavy species. It is

Fig. 2: Simulation of a MIPAS spectrum. The broad spectral domain as well as the high resolution allows one to observe separately the emission of a large number of molecules. (Courtesy of M. Endemann, ESA)

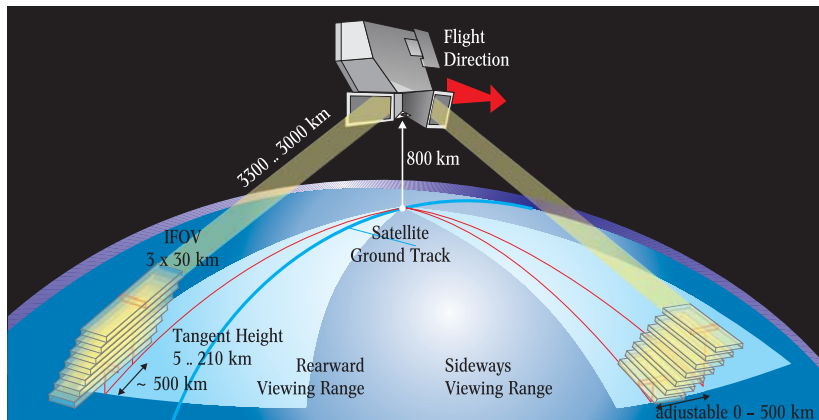
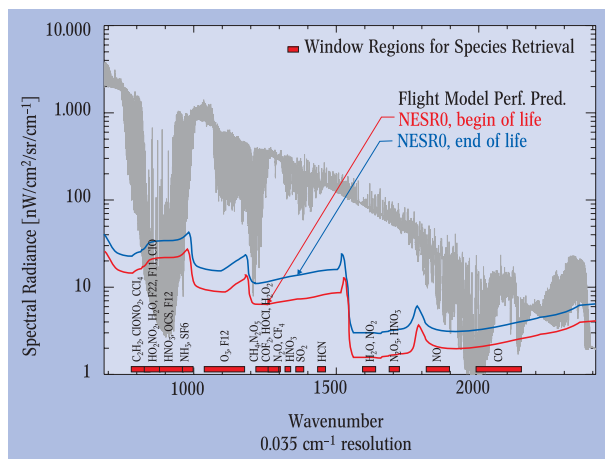


Fig. 3: Observational modes of MIPAS. The nominal mode is rearward viewing, but there is also a sideways viewing mode dedicated to the study of specific problems such as a volcano eruption (see text). (courtesy of M. Endemann, ESA)

not the goal of this paper to give a complete review of all these questions but rather to show on a few selected examples that up-to-date laboratory spectroscopic methods are required to meet the needs of atmospheric physics. The paper is organised as follows: After a short presentation of a remote sensing satellite experiment and its needs, we will concentrate on real examples linked to the „challenging spectroscopic questions“ quoted above. The case of the HOCl molecule for which simultaneous measurements in two different spectral regions were required to derive realistic intensities will be described first. Then we will discuss a case for heavy species. Indeed, the absorption of such species appears as a quasi-continuum in the atmospheric spectra and there are two „schools of thought“: either to measure all desired absorption cross sections for the whole range of atmospheric pressures and temperatures or to make some effort to model and generate a synthetic vibration-rotation spectrum. As an example the case of the ClONO₂ molecule will be described.

The MIPAS Experiment

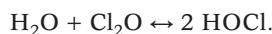
The MIPAS (Michelson Interferometer for Passive Atmospheric Sounding) is a core instrument of the European Space Agency and is part of the ENVISAT sa-

tellite successfully launched by an ARIANE 5 rocket recently. Figure 1 presents a general view of the ENVISAT satellite with some of the various experiments. Three of them are devoted to the observation of the atmosphere. They are GOMOS (Global Ozone Monitoring by Occultation of Stars), SCIAMACHY (Scanning Imaging Absorption spectroMeter for Atmospheric CHartography) working in the ultra-violet, visible and near infrared spectral ranges and MIPAS working in the thermal infrared. More precisely, MIPAS is a high resolution Fourier transform interferometer measuring the emission of the atmosphere in the 4.15 – 14.6 μm spectral region where the atmospheric emission is significant. Note that besides its capability to provide broadband atmospheric spectra, its resolution (0.05 cm⁻¹ apodised) is suitable for spectroscopic characterization since it allows one to resolve the spectroscopic features of most atmospheric constituents. Figure 2 presents a simulation of an atmospheric spectrum as it should be observed by MIPAS. Besides the most abundant minor atmospheric constituents such as CO₂, H₂O, O₃, CH₄... whose emission is strong, thanks to the broad band coverage and the high resolution it will be possible to also observe a number of less abundant species such as NO₂, HNO₃, ClONO₂, ... which are involved in the destruction processes of the ozone molecule and whose measurement is crucial to assess the validity of the photochemical atmospheric models. The pointing geometry (see Fig. 3) is dual. The nominal mode is a rear viewing geometry allowing one to record at a vertical resolution of about 3 km spectra covering an altitude range going from about 6–8 km to about 55 km leading to the determination of well resolved vertical profiles of a number of species (see Fig. 2). There exists also a distinct mode, the sideways viewing mode, dedicated to the measurement of unexpected events such as volcanic eruptions, to the monitoring of crowded aircraft routes over the Atlantic or Pacific oceans or to the study of day-night transitions. Obviously the analysis of the MIPAS atmospheric spectra and the retrieval of accurate vertical concentration profiles require a precise knowledge of the spectral parameters of a lot of species. As already stressed it is not the goal of this paper to discuss all the problems faced by experimental and theoretical spectroscopy to provide such data but to concentrate on two characteristics examples, namely the case of an unstable molecule such as HOCl and of a heavy species such as ClONO₂.

Line intensities for an unstable molecule: HOCl

The chemical processes involving chlorine atoms are believed to be a very important path leading to the depletion of ozone in the stratosphere. Among the molecules taking part in these processes, hypochlorous acid HOCl is considered to be a temporary reservoir of chlorine atoms and has been detected in the atmosphere at mid-latitudes by far infrared emission. Because it lies in an atmospheric window (see Fig. 2), the ν₂ band can also be used to detect HOCl in the stratosphere. Indeed, this band was used, for example, to measure the column abundance of HOCl over the Antarctic [1] and to estimate the mixing ratio of HOCl in the Arctic stratosphere using MIPAS-balloon limb emission spectra [2]. However the accuracy of the results of such measurements depends heavily on the quality of the line intensities used for the retrievals. The main challen-

ge when aiming at the laboratory measurement of *absolute* intensities for unstable species like hypochlorous acid lies in the accurate determination of their abundances. Indeed, HOCl always exists in the following equilibrium:



Various methods were used in the literature to determine the concentration of HOCl: For example, chemical titrations or modelling of the UV photolysis or using the UV absorption cross-sections of HOCl. However as can be seen in Fig. 4 the band intensities of the ν_2 band derived by these methods show a large scattering. In order to solve the problem of the determination of the HOCl concentration it was decided to rely on a new method [6] based on the determination of the HOCl concentration in the sample using line strengths in the pure rotational spectrum since the permanent dipole moment of the molecule can be derived from frequency measurements (Stark effect) without knowing the concentration of the molecule in the cell. Then using this dipole moment derived in this manner and an adequate intensity model it is possible to calculate the absolute line intensities of the pure rotation band which absorbs in the far infrared (FIR). The ratio of the measured intensity of pure rotation lines to their absolute intensity, calculated as described above, yields directly the desired concentration. Figure 5 presents a schematics of the experimental setup which was used: The FIR lines and the ν_2 lines are simultaneously measured using a Fourier transform interferometer and a tunable diode laser spectrometer respectively. The band intensity derived using this method is given in Fig. 4: it is easy to see that it is rather different from the previous determinations. The individual line intensities of the ν_2 band were also calculated and compared (Tab. 1) to the values given in the HITRAN atmospheric database [7]. It appears clearly that the intensity values included in this database are overestimated by an amount of about 40 %. As a consequence, using the HITRAN values to retrieve the HOCl concentrations in the atmosphere would lead to an underestimation of these concentrations by about the same amount of 40 %.

This example shows clearly that, when measuring line intensities of unstable molecules in the laboratory, one has to be very careful to determine properly the gas concentration in the cell. The approach consisting in performing simultaneous line intensity measurements proves to be very powerful. On the one hand one measures in the band of interest and on the other hand in the rotational spectrum where the absolute intensities can be calculated properly and subsequently used to determine the species concentration in the sample. Such a method is obviously promising and of great interest in the atmospheric and astrophysical contexts because many of the constituents involved are unstable.

Line by Line simulation of the spectrum of a heavy molecule: ClONO₂

Chlorine nitrate, ClONO₂, which serves as a temporary reservoir species for chlorine and nitrogen radicals, plays an important role in stratospheric ozone chemistry. It has been detected and measured in the stratosphere in different infrared spectral regions from various platforms (ground, aircraft, balloons, space)

and using either absorption or emission techniques. However up to now the analysis of the atmospheric spectra was performed using absorption cross sections since no good line-by-line spectrum was available. Indeed, at room temperature, even at high resolution, the bands are barely resolved due to the weak values of the rotational constants and the overlapping of lines of the two isotopomers as well as from several hot bands. As a consequence, the corresponding absorptions appear

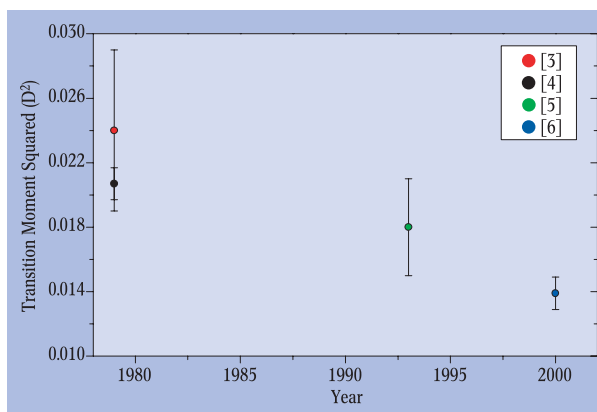


Fig. 4: HOCl ν_2 band intensities. Only the band intensity derived by Vander Auwera et al. [6] is based on simultaneous intensity measurements in two different spectral regions allowing a precise determination of the HOCl abundance in the cell (see text).

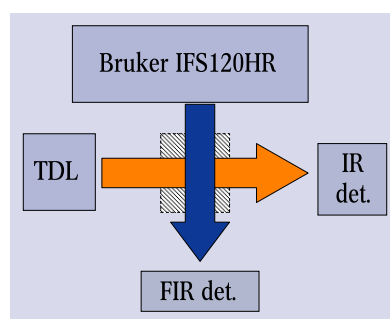


Fig. 5: Schematics of the experimental setup used to measure HOCl ν_2 line intensities. The Bruker FTS was used to measure the far infrared rotational spectrum of HOCl and to determine the concentration of HOCl in the sample (see text). The tunable diode laser (TDL) spectrometer was used to measure the line intensities in the ν_2 band. Simultaneous measurement in both channels is essential.

ν_2 Band of HOCl: Comparison of line intensities for the transition $1_{01} \leftrightarrow 2_{02}$

	ν (cm ⁻¹)	Int $\times 10^{21}$	Ratio
³⁷ Cl	1236.1622 [6]	1.41	
	1236.1617 [7]	2.42	0.58
³⁵ Cl	1236.6309 [6]	4.44	
	1236.6304 [7]	7.54	0.59

Tab. 1: ν_2 band of HOCl: Comparison of line intensities for the transition $1_{01} \leftrightarrow 2_{02}$. When used in the retrieval processes the new intensities would lead to an HOCl atmospheric concentration about 40 % higher than that obtained using the values quoted in the HITRAN database [7]. Intensities are given in cm⁻¹/(molecule cm⁻²) at 296 K

as pseudo-continua. One possibility is then, as far as laboratory measurements are concerned, to measure the corresponding cross sections at various temperatures and various air-pressures spanning the atmospheric temperature and pressure ranges. This is an extremely tedious and difficult task. In fact, the measurements are performed for a finite set of temperatures and pressures and the measured cross sections are then interpolated and/or extrapolated for the analysis of the atmospheric spectra. This is usually not totally satisfactory as compared to a line-by-line calculation which allows one to account properly for temperature and air-pressure variations. However, for all the reasons above, it is quite a challenge to generate a line list for such a

heavy molecule like ClONO_2 . In fact, as a good starting point for a high resolution spectroscopic analysis of this species, one has to have a fully resolved spectrum. It is only recently that such spectra have become available through the use of a molecular beam and a tunable diode laser spectrometer [8, 9]. The low temperatures (-7 – 30 K) obtained in the beam studies greatly simplified the spectrum (the hot bands as well as the transitions involving excited rotational levels vanish almost completely) thus allowing complete ro-vibrational assignment. Do such studies provide enough results to model atmospheric or room temperature spectra? Unfortunately not since only levels with low J and K_a rotational quantum numbers are observed at the beam temperatures and since extrapolation to the high J and K_a values required for modelling atmospheric spectra proves to be inaccurate. Figures 6 and 7 give a comparison between the Q-branches of the ν_4 bands of the ^{35}Cl and ^{37}Cl isotopic variants of chlorine nitrate recorded by Fourier transform spectroscopy at 190 K [10] and simulated using the Hamiltonian constants derived from the analysis of the molecular beam

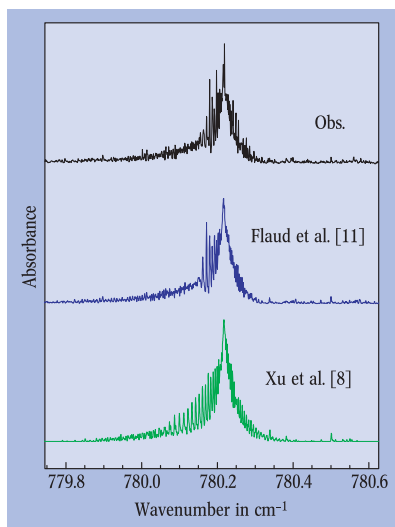


Fig. 6: Comparison of the observed and simulated ν_4 Q-branches of $^{35}\text{ClONO}_2$. The lowest curve is obtained using the Hamiltonian constants which were derived from the analysis of very low temperature beam spectra illustrating the difficulty in extrapolating to stratospheric temperatures. The middle curve shows the improvement obtained by the new analysis.

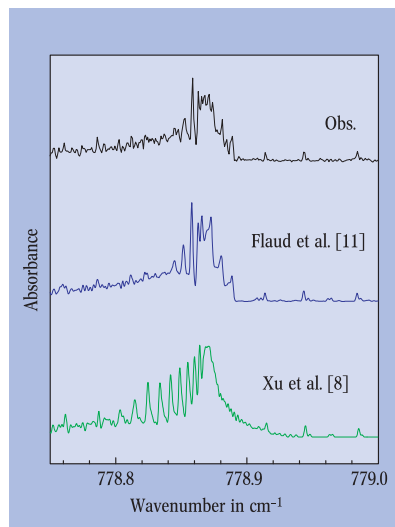


Fig. 7: Comparison of the observed and simulated ν_4 Q-branches of $^{37}\text{ClONO}_2$. The lowest curve is obtained using the Hamiltonian constants which were derived from the analysis of very low temperature beam spectra illustrating the difficulty in extrapolating to stratospheric temperatures. The middle curve shows the improvement obtained by the new analysis.

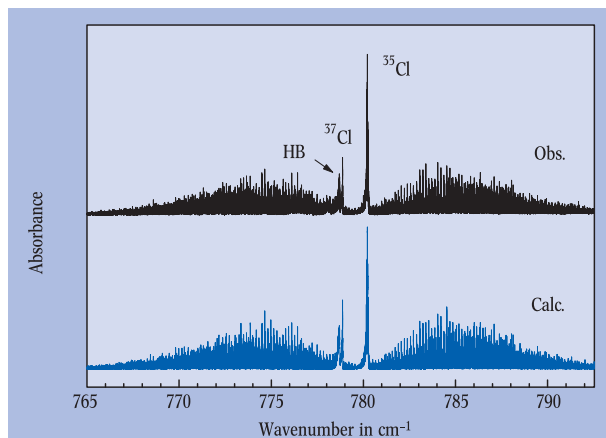


Fig. 8: Simulation of the entire ν_4 band including both isotopic species and the first hot band of $^{35}\text{ClONO}_2$.

spectra. It is obvious that in both cases the simulations do not permit a satisfactory reproduction of the observed spectra. Therefore it is necessary to assign spectra recorded at temperatures much higher than those encountered in a molecular beam. Such a spectrum was recorded at very high resolution (better than 10^{-3} cm^{-1}) and a temperature of 190 K with a Fourier transform spectrometer [10]. However despite the high resolution the assignment process proved to be difficult for various reasons:

- ▶ Given the existence of low-lying vibrational states, a number of hot bands appear in the spectrum even at a temperature of 190 K.
- ▶ Two isotopomers (^{35}Cl and ^{37}Cl) are absorbing.
- ▶ Resonance effects perturb the energy level patterns.

It is not the goal of this paper to describe extensively the assignment process but it is important to stress that it was started concentrating on the ν_4 cold band of $^{35}\text{ClONO}_2$. In fact, this band is the strongest one in the 780 cm^{-1} spectral region and, with the aid of the upper state constants of Xu et al. [8], which proved to be essential to start the analysis, it was possible to assign the low J and K_a transitions in the P- and R-branches. The extrapolation to high J and K_a values was difficult; however, eventually, we were able to reach rather high values of these quantum numbers. Then using a Hamiltonian model taking into account the relevant vib-rotational resonances with other states a much better simulation of the Fourier transform spectrum was achieved (see Fig. 6). An analogous procedure was followed for the ν_4 band of the ^{37}Cl isotopomer and again, as shown in Fig. 7, the Q-branch of this band was much better modelled. Finally as seen in Fig. 8 one can notice the very good overall agreement between the observed and simulated spectra.

The ultimate goal of a thorough spectroscopic study of the ClONO_2 spectrum would be to generate a complete line listing of all the bands absorbing in the spectral range of interest, i. e. in the 780 cm^{-1} spectral region in this case. Unfortunately such a goal is nearly out of reach since ClONO_2 possesses several low-lying vibrational states. However, if in a narrow spectral range around the ν_4 Q-branch appropriate for atmospheric retrievals, the absorption can be modelled by a line-by-line calculation plus a pseudo-continuum depending only on temperature, then the analysis of the atmospheric spectra and the retrieval of the ClONO_2 abundance would be greatly facilitated. Such an approach proved to be possible by systematically comparing synthetic spectra generated using the Hamiltonian constants derived from the analysis of the Fourier transform spectrum to the recent cross section measurements of Birk and Wagner, [10]. Fig. 9 gives an example for comparison at a temperature of 218 K between observed and calculated spectra in the region 779 – 781 cm^{-1} where the ν_4 Q-branch of $^{35}\text{ClONO}_2$ which is widely used in atmospheric retrievals appears. One can see the excellent agreement achieved.

Such an example shows that mixing up-to-date high resolution experimental techniques (molecular beam and tunable diode laser spectroscopy, high resolution Fourier transform spectroscopy) with sophisticated theoretical models taking into account the various resonances leads to the unexpected result that the pseudo-continuum exhibited by a heavy molecule can be modelled through a line-by-line calculation.

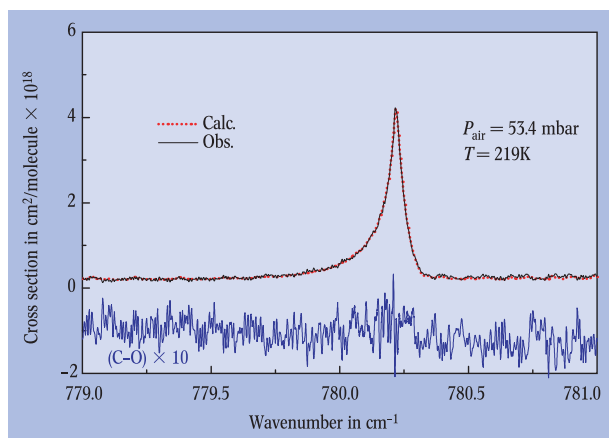


Fig. 9: Modelling of the ν_4 Q-branch region of $^{35}\text{ClONO}_2$ at 219 K. Note the good agreement as shown by the residuals given at the bottom of the figure.

Conclusion

It was not the goal of this paper to give a complete overview of infrared spectroscopy applied to atmospheric measurements or of the various techniques used to probe the atmosphere but rather to show a few selected examples of recent progress, both experimental and theoretical, achieved by modern molecular spectroscopy. Indeed it was shown that, to provide the accurate spectral parameters required for the analysis of atmospheric spectra, it is necessary to use the best experimental techniques in the laboratory as well as sophisticated theoretical models. Two examples of studies in which the author was involved, were chosen. First the HOCl unstable molecule for which it proved necessary to perform simultaneous measurements in two different spectral regions to get accurate absolute line intensities. Second the heavy ClONO₂ molecule for which it was possible, using high resolution experimental techniques coupled to a molecular beam and an appropriate theoretical model, to generate a synthetic line spectrum in order to model the pseudo-continuum absorption observed in normal conditions for this molecule. It is hoped that the reader will be convinced that molecular spectroscopy is a lively scientific field whose future is certain since there is still much of work and progress to be made in order to meet the requirements of a number of fields (Atmospheric physics and chemistry, astrophysics, atmospheres of the planets, combustions,...).

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