The $H_X N_Y O_Z$ family

M. HERMAN
Laboratoire de Chimie Physique Moléculaire
Université Libre de Bruxelles
Belgium

Species made of nitrogen and oxygen ($N_Y O_Z$) are of course known to exist. The simplest ones, NO, NO_2 and N_2O were extensively studied and their geometry was characterized. NO_3, N_2O_2, N_2O_4, N_2O_3 and N_2O_5 were observed, but their structural and sometimes chemical properties remain to be well characterized. One can even postulate the existence of other larger species fitting the chemical formula $N_Y O_Z$.

In the presence of water (H_2O), the $N_Y O_Z$ species react with each other and form an extensive system with a lot of chemical interplays. Indeed, several chemical equilibria take place, resulting into the formation of new, although connected species, as nitrous acid ($HONO$) or nitric acid (HNO_3).

Most of the related reactions are such that the species coexist each in reasonable abundance under a wide range of experimental conditions. It turns out that the role of the $H_X N_Y O_Z$ species is central in various master physico-chemical processes occurring in our atmosphere. Thus the study of that chemical family as a whole is meaningful. It is actually of fundamental importance not only in the environmental context, but also in various other up-to-date chemical areas, such as those dealing with combustion, energy transfers or chemical bondings.

The basic role of infrared spectroscopy in probing the $H_X N_Y O_Z$ molecules is well established, in particular in the atmospheric area. A lot of work remain however to be performed. Our recent contribution in that context aiming both at the spectroscopy and the chemistry of those species will be detailed. Our achievements include high resolution Fourier transform experiments of line positions and intensities, in some cases using a supersonic expansion. $HONO$ and N_2O_4 will be the main targets of the talk.

Tunable Diode Laser Spectroscopy. New Methods and Applications

A.I. NADEZHDINSKY

Millimeter -wave and Far Infrared Spectrum of CHF_2Cl.

G. Cazzoli, L. Cludi, G. Cotti, C. Degli Esposti

Dipartimento di Chimica "G. Ciamician" dell'Universita' di Bologna, Via Selmi 2, 40126 Bologna Italy.

A. Guarnieri

Abteilung Chemische Physik im Institut fur Physikalische Chemie der Universitat Kiel Olshausenstr. 40-60, D-2300 Kiel 1, Federal Republic of Germany.

Chlorodifluoromethane (HCFC-22) is the simplest chlorofluorocarbon molecule suggested as an alternative to the chlorofluorocarbon (CFC) molecules up to now used. This alternative allows a better protection of the ozone layer and also reduces the contribution to the global warming.

The eventual detection and monitoring of this molecule in the atmosphere by spectroscopic technique requires accurate laboratory data and so we decided to observe the rotational spectrum of CHF_2Cl in the millimeter-wave and in the FIR region up to 1260 GHz by using a conventional millimeter-wave spectrometer and a FIR laser side band spectrometer respectively.

The centrifugal distortion analysis of the spectrum has been performed using the A and S reduction of the rotational Hamiltonian. The results of the analysis will be reported and compared with those available in literature.

Measurements of the self broadening and of the pressure broadening with nitrogen and oxygen of rotational transitions have been also made and an appreciable dependence on J of the pressure broadening coefficients has been observed.

Double Modulation Sideband Spectroscopie

W.A.Kreiner, W.Höhe, A. Ainetschian, and U. Häring

Modulation of CO_2 laser radiation at microwave frequencies is a well established technique to obtain narrowband tunable infrared radiation. Combining the microwave with radio frequency leads to the occurrence of several sidebands instead of one. These IR frequencies are spaced by about 1 MHz and can be used to perform IR/IR double resonance on levels split due to the Stark effect. We have investigated the SiF_4 molecule and have determined several dipole moment parameters from the linear effect. Investigation of the quadratic effect is in progress. We have observed the $K = 3$ splitting on the NF_3 molecule with conventional IR saturation spectroscopy. From resolution of the quadrupole hyperfine structure we have obtained improved values for the coupling constants.

THEORETICAL APPROACH OF THE ROTATIONAL ENERGY LEVELS OF SiC$_2$

L. H. COUDERT

Laboratoire de Physique Moléculaire et Applications
Université Pierre et Marie Curie et CNRS, Boite 76
4, Place Jussieu, 75252 Paris Cedex 05, France

In the T-shaped SiC$_2$ molecule, it is conjectured that the silicium atom is weakly bound to the C$_2$ fragment by an ionic essentially non directional bound, and thus could migrate around the C$_2$ fragment.[1] The ν_3 mode in SiC$_2$, corresponding to this motion, might, therefore, be a large amplitude motion and this could explain the difficulties encountered in fitting the microwave spectrum of this molecule in the ground vibrational state[2] as well as in the $v_3 = 1$ vibrational state.[1]

In this paper, a formalism is derived in which the large amplitude ν_3 mode and the three degrees of freedom corresponding to the overall rotation of the molecule are treated simultaneously. This formalism accounts for the two main features of the SiC$_2$ dynamics: the fact that the A rotational constant goes to infinity for a linear configuration of the molecule and the Coriolis coupling between the large amplitude ν_3 mode and the rotation. A rovibrational Hamiltonian is derived and it is shown that, taking a simple model potential function, it can be diagonalized taking into account $\Delta v_3 > 0$ and $\Delta K > 0$ matrix elements.

Attempts are being made to gain further information about the molecule internal dynamics and, introducing distortion-like terms in the Hamiltonian, to reproduce the microwave data[1,2] within their experimental uncertainty.

[1] M. Bogey, C. Demuynck, J.-L. Destombes and A. D. Walters, Astron. Astrophys. **247**, L13-L16 (1991).

[2] C. A. Gottlieb, J. M. Vrtilek and P. Thaddeus, Astrophysical Journal **343**, L29-L32 (1989).

What You Thought You Already Knew about the Bending Motion of Triatomic Molecules

Wolfgang Quapp[1]
Brenda P. Winnewisser[2]

[1] *Mathematisches Institut, Universität Leipzig, Germany*
[2] *Physikalisch-Chemisches Institut der Justus-Liebig-Universität,*
Heinrich-Buff-Ring 58, W-6300 Gießen, Germany

We have found that chemists, physicists and mathematicians frequently have conceptual difficulties when first confronted with the subject of the dynamics of the bending of triatomic molecules. The present treatment is the result of our efforts to deal with the hidden assumptions and frequent misconceptions associated with this apparently simple problem; a subject in molecular physics which is, in principle, mathematically solved.

The bending vibrations of linear, quasilinear, and bent molecules are qualitatively different phenomena. Each of these cases has been fully described by quantum mechanical formulations in the last half century, but important two-dimensional aspects of all three cases, and the relationship between the three types of bending behavior remain difficult to visualize. Simple two-dimensional figures can help to give an introduction to basic spatial and mathematical aspects of the bending problem.