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RUDOLPH A. MARCUS (*)

THEORY AND EXPERIMENT IN CHEMICAL REACTIONS: ELECTRON TRANSFERS AND UNIMOLECULAR REACTIONS

INTRODUCTORY REMARKS

It is indeed a pleasure and an honor to introduce this interesting and timely symposium of the Accademia dei Lincei, «From Elementary Processes to Complex Systems». The topics in the title of my lecture are intended to exemplify this theme. Originally, I had planned to illustrate the lecture with examples drawn from several of my own experiences and those of my research group on the interaction of theory and experiment – electron transfer processes [1], unimolecular reactions of isolated molecules in the gas phase [2, 3], and intramolecular dynamics in isolated molecules, and inferred from high resolution spectroscopic measurements [4, 5]. Upon further reflection it seemed best instead to focus in the lecture itself only on one subject, the first topic but, in the written version, give a brief description also of some aspects of the other two topics.

The studies of unimolecular reactions which I would have liked to discuss include both reaction rates [2] and the measurement of the distribution of the rotational-vibrational quantum states of their reaction products [3]. The high resolution spectroscopic studies [4, 5] include analyses of several systems – the two-photon Doppler free spectroscopy of benzene, below and within the so-called «channel three» energy region [4], the CH overtone spectra [5] of $(CX_3)_3\,YC \equiv CH$, where X is H or D and Y is C or Si, and the CH overtone spectrum [5] of benzene ($v_{CH} = 1$ to 3).

In the case of unimolecular reactions, recent experiments have focused on the dependence of the rates of unimolecular reactions (dissociations or isomerizations) of isolated molecules on the vibrational energy of those molecules. Such studies took a major step forward with the introduction of lasers to photoexcite the molecules. In those studies, the amount of energy that the resulting

(*) Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, CA 91125 (USA).

high energy molecule possesses becomes more precisely known. The complexity here was one of technology – the new experiments were technologically more complex than experimental studies of thermal or photochemical kinetics of molecules in bulbs as a function of temperature and pressure.

More recently, a further increase in complexity in the study of unimolecular reactions occurred – detailed supplementary information on these reactions, namely, on the distribution of the quantum states of the reaction products, has been obtained. Such extra detail is demanding of any theory, and in turn provides new information on the dissociation process itself. Both in these experiments and in those on unimolecular reaction rates, the use of cold molecular beams has played an important role. To treat these experimental results for a particular class of unimolecular reactions, we were able to extend RRKM theory, which previously had been designed to treat only the energy-dependent reaction rates in unimolecular reactions. In this extension, a dynamical assumption was added about the behavior of the fragments of the unimolecular dissociation products en route from the transition state to their finally separated state.

In the fields of high resolution vibronic and vibrational-rotational spectroscopy there has also been an additional increase in complexity, both in the molecules themselves and in the detailed level of information learned. In no small measure this step was also made possible by the introduction of lasers. In earlier detailed spectroscopic studies of molecules having excess energy, attention was focused on small molecules, but now molecules such as benzene with its thirty vibrations and those such as $(CX_3)_3\,YC \equiv CH$ with its forty-two vibrations have been studied, both experimentally and theoretically. In a recent quantum mechanical treatment [4, 5] potentially millions of quantum states (zeroth-order quantum states) of the nuclear motion can contribute to the observed phenomena and complicate by sheer numbers a theoretical treatment. Among other things, elementary «artificial intelligence» searching techniques were used to select from them the most important contributing states [4, 5].

However, the main subject of my lecture in this symposium is the field of electron transfer processes and its remarkable development in recent decades. It indeed provides a timely example of the progress from elementary processes to complex systems. In the late 1940s and the 1950s, the main focus was on the study of isotopic exchange reactions (as in reaction 3 and fig. 3 in the following reprint of my Nobel Lecture). They represent a very simple type of process, and form what is probably the simplest class of reactions in chemistry. Detailed studies in the field have now been extended to much more complex systems, such as the photosynthetic reaction center (fig. 11 in the following lecture) and other proteins, such as cytochrome c. The lecture which I present at this symposium is taken from the Nobel Lecture [1] and describes the progress made along this path from simple to complex systems. I have also added some pictu-

res selected from the poster which the Royal Swedish Academy of Sciences prepares each year, in this case 1992, as part of the Nobel Prize ceremonies, and have added one taken from the poster for the 1988 prize in chemistry (the originals were in color).

References

[1] *Electron Transfer Reactions in Chemistry: Theory and Experiment*, R. A. Marcus, in *Les Prix Nobel*, T. Frangsmyr, ed., Nobel Foundation (Almqvist & Wiksell, Stockholm, Sweden 1993) p. 63, reprinted in the following article.

[2] *On the Statistical Theory of Unimolecular Processes*, D. M. Wardlaw and R. A. Marcus, «Adv. Chem. Phys.» **70**, Part 2, 231 (1987); *Application of Unimolecular Reaction Rate Theory for Highly Flexible Transition States to the Dissociation of* CH_2CO *into* CH_2 *and* CO, S. J. Klippenstein and R. A. Marcus, «J. Chem. Phys.» **91**, 2280 (1989), and references cited therein.

[3] *Application of Unimolecular Reaction Rate Theory for Highly Flexible Transition States to the Dissociation of* CH_2CO *into* CH_2 *and* CO. II. *Photofragment Excitation Spectra for Vibrationally-Excited Fragments*, S. J. Klippenstein and R. A. Marcus, «J. Chem. Phys.» **93**, 2418 (1990) and references cited therein.

[4] *Theory of Anharmonically-Modified Coriolis Coupling in the* S_1 *State of Benzene and Relation to Experiment*, A. Helman and R. A. Marcus, «J. Chem. Phys.» **95**, 872 (1991); *Theory of Fluorescence Excitation Spectra Using Anharmonic-Coriolis Coupling in* S_1 *and Internal Conversion to* S_0. II. *Application to the Channel Three Problem in Benzene for the* $14^1 1^2$ *Band*, A. Helman and R. A. Marcus, «J. Chem. Phys.» **99**, 5002 (1993), and references cited therein.

[5] *Theoretical Study of Intramolecular Vibrational Relaxation of Acetylenic* CH *Vibration for* $v = 1$ *and 2 in Large Polyatomic Molecules* $(CX_3)_3YCCH$, *where* X = H *or* D, Y = C *or* Si, A. A. Stuchebrukhov and R. A. Marcus, «J. Chem. Phys.» **98**, 6044 (1993); *Vibrational Superexchange Mechanism of Intramolecular Vibrational Relaxation in* $(CH_3)_3CCCH$ *molecules*, A. A. Stuchefrukhov, A. Mehta, and R. A. Marcus, «J. Phys. Chem.» **97**, 12491 (1993); *Intramolecular Dynamics III. Theoretical Studies of the* CH *overtone Spectra for Benzene*, Y.-F. Zhang and R. A. Marcus, «J. Chem. Phys.», **97**, 5283 (1992).