1. INTRODUCTION

The first meeting of the International Symposium on Free Radicals (ISFR) was held in 1956 in Canada, organized by Paul A. Giguère (Laval University, Québec). Since then, the ISFR sessions have been held across the world, and scientists have shared cutting-edge research and perspectives that have driven our understanding of free radicals in a variety of contexts, including our atmosphere, interstellar environments, and combustion. The recent (35th) ISFR was held for the first time in mainland China, along the Qiantang River in the beautiful and prosperous city of Hangzhou, from September 15th to 20th, 2019. The five-day symposium was cochaired by Xuming Yang (Dalian Institute of Chemical Physics, Chinese Academy of Science) and Jingsong Zhang (University of California, Riverside), and it featured presentations from distinguished researchers from over 14 countries. The sessions were compartmentalized into seven main themes, as outlined in Table 1 with respective session chairs denoted.

The conference commenced by acknowledging the International Symposium on Free Radicals (ISFR) Broida prize winner. The Broida prize is named after Dr. Herbert P. Broida (1920–1978), who was an American physics professor at the University of California, Santa Barbara. Dr. Broida was instrumental in establishing a program at the National Bureau of Standards for the spectroscopic study of free radicals using the matrix isolation technique, and he was one of the first to employ lasers to perform molecular spectroscopy. He was also one of the earliest chairs of the symposium. At the 35th ISFR, the prize was awarded to Xingan Wang (University of Science and Technology of China) for his seminal contributions to the experimental study of the geometric phase effects in chemical reactions using the near threshold ionization, velocity map imaging technique.

2. REACTION DYNAMICS

Xingan Wang (University of Science and Technology of China, China) discussed the dynamics of the H + HD and F + HD reactions. The reactions were studied using a crossed molecular beam (CMB) apparatus equipped with a time sliced velocity map ion imaging (VMI) detector. Additionally, a resonance-enhanced 1 + 1′ (VUV + UV) near threshold ionization scheme (REMPI) was employed to acquire high-resolution ion images, at the rotational level, for the H + HD reaction [Nat. Chem. 2018, 10, 653. DOI: 10.1038/s41557-018-0032-9]. Through this technique, angular oscillations in differential cross sections (DCS) were observed. These results can be compared with the predictions of high level calculations and contribute to the understanding of quantum effects in these types of scattering experiments.

Astrid Bergcat (Institut des Sciences Moléculaires, University of Bordeaux, France) presented the results of CMB experiments that were conducted to study the O + O₂ isotopic exchange reaction, which is important for understanding the isotope effects in ozone. Although it is known that ozone is predominantly formed through the simple recombination reaction O + O₁ → O₂ there is a significant enrichment of both O¹⁷O and O¹⁸O in O₃ that is still not well understood. A current explanation invokes the thermodynamics of two exchange reactions, O¹⁸O + O₁₆O₂ → O₁₆O + O¹⁸O (exothermic) and O¹⁸O + O₁₈O₂ → O₁₈O + O¹⁸O¹⁶O (endothermic). By using a variable crossing angle, the integral cross sections were able to be measured as a function of the relative translational energy.

Hongwei Li (Suits Group, University of Missouri, USA) discussed roaming-mediated inter-system crossing (ISC) in the exit channel of the $O(3P) +$ alkylamine (dimethylamine and trimethylamine) reactions. In CMB experiments, $O(3P)$ abstracts a hydrogen from the alkylamine to produce an OH radical and an aminoalkyl radical [Nat. Chem. 2019, 11, 123. DOI: 10.1038/s41557-018-0186-5]. The low translational-energy release and isotropic angular distributions of the products indicate that the reactions undergo formation of a long-lived complex prior to formation of the detected products. Theory does not predict a deep well on the triplet potential energy surface (PES) that could support such a complex. However, the singlet PES has a deep exit channel well before OH elimination. It is suggested that ISC occurs in the exit-channel region due to the long-range dipole–dipole interaction between the nascent radical product pair coupled with the vanishing singlet–triplet splitting and strong spin–orbit coupling.

Donghui Zhang (Dalian Institute of Chemical Physics, China) discussed quantum dynamics simulations for the $F + H_2O/CH_4$ reaction. The Fundamental Invariant Neural Network (FI-NN) method was used to calculate accurate PESs with the proper permutational symmetry. Using the calculated PESs, the time-dependent wavepacket method was then employed to study the dynamics of these reactions at the state-to-state level. From these predictions, the relevant dynamic resonances and the effects of vibrational excitation on these reactions were modeled.

Piergiorgio Casavecchia (University of Perugia, Italy) discussed the reaction dynamics of $O(3P)$ with 1-butene and 1,2-butadiene. Reactions of $O(3P)$ with unsaturated hydrocarbons are important oxidation mechanisms in combustion processes. These reactions can have a variety of product channels, including some that can only occur via ISC. CMB experiments are well suited for studying these types of reactions and have previously been employed to study the reactions of $O(3P)$ with smaller unsaturated hydrocarbons (acetylene, ethylene, propene, allene, and propyne) [Chem. Soc. Rev. 2017, 46, 7517. DOI: 10.1039/c7cs00601b]. In this presentation, results of CMB experiments involving larger unsaturated hydrocarbons (1-butene and 1,2-butadiene) were discussed [Chem. Phys. Lett. 2017, 683, 105. DOI: 10.1016/j.cplett.2017.02.036; Chin. J. Chem. Phys. 2019, 32, 113. DOI: 10.1063/1674-0068/cjcp1812281; J. Phys. Chem. A 2019, 123, 9934. DOI: 10.1021/acs.jpca.9b07621]. They were able to compare their results against theoretical predictions and explore how product distributions, branching ratios, and the role of ISC vary with increasing molecular complexity.

György Lendvay (Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Hungary) discussed theoretical studies of the dynamics of the $O + O_2 \rightarrow O^+O + O$ and $HO + HI \rightarrow H_2O + I$ reactions. Reaction cross sections and thermal rate coefficients were predicted using quasiclassical trajectory calculations on the relevant PESs. For the first reaction, a new mechanism has been identified at very high collision energies: the reacting system does not enter the potential well corresponding to the $O_3$ complex [J. Phys. Chem. A 2019, 123, 10230. DOI: 10.1021/acs.jpca.9b07393]. And for the second reaction, the $OH + HI$ reaction was found to be faster than its HBr analog.

Hua Guo (University of New Mexico, USA) presented theory results on the nonadiabatic photodissociation dynamics of ammonia, the hydroxymethyl radical, and phenol. Because these processes break the Born–Oppenheimer approximation (BOA), they were required to calculate diabatic potential energy matrices to carry out full- and reduced-dimensional quantum dynamic calculations. The calculations led to predictions of absorption spectra, species lifetimes, and product state distributions, which were compared against experimental results, thus providing insights into nonadiabatic dynamics.

Chunlei Xiao (State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China) presented results on the dynamics of the $H + HD \rightarrow H_2 + D$ reaction. The experiments were conducted using an H-tagging CMB apparatus to measure collision energy dependent DCSs for specific $H_2$ product states. By comparing the experimental results with predictions from calculations, they were able to study the geometric phase (GP) effects of the reaction in various ways. Previous experiments [Science 2018, 362, 1289. DOI: 10.1126/science.aav1356] enabled observation of GP effects at an energy 0.24 eV above the conical intersection (CI), whereas in the current work, GP effects were still observable at an energy 0.4 eV below the CI. They also prepared vibrationally excited HD molecules with preferential alignment and observed a significant difference in the rotational state distribution of the $H_2$ product in the forward scattering direction with and without the inclusion of GP.

Shan Xi Tian (University of Science and Technology of China, China) presented results on the ion–molecule charge exchange reactions between Ar$^+$ and various small molecules (NO, CO$_2$, N$_2$, and O$_2$). The dynamics of these charge transfer reactions were studied using a CMB apparatus coupled with VMI [J. Phys. Chem. A 2018, 122, 9171. DOI: 10.1021/acs.jpca.8b08005; J. Phys. Chem. A 2019, 123, 8536. DOI: 10.1021/acs.jpca.9b06607]. Each of these reactions can produce electronically excited products. However, the excited state distributions are different for each reaction and depend upon the initial collision energies. Additionally, the angular distributions of the products of each reaction are different, indicating significant complexity in these charge exchange dynamics. The results of these experiments may provide excellent benchmarks for theoretical predictions.

Richard Thomas (Stockholm University, Sweden) utilized the double electrostatic ion ring experiment (DESIREE) facility to study charge transfer reactions and mutual neutralization reactions between merged beams of cations and anions. The DESIREE facility allows the study of the interactions between cations and anions at temperatures as low as 10 K and collision energies as low as 10 meV [Rev. Sci. Instrum. 2011, 82, 065112. DOI: 10.1063/1.3602928; Rev. Sci. Instrum. 2013, 84, 055115. DOI: 10.1063/1.4877072]. Preliminary results were presented on reactions of $F^+ + CL^-$ to form either $F + CL$ (mutual neutralization, MN: a single electron transfer process) or $F^+ + CL^+$ (a double electron transfer process). The results of the experiment gave no indication of the double charge transfer process occurring. For MN, analysis of the kinetic energies of the neutral F and Cl products is consistent with the reaction mostly proceeding...
through the formation of ground state fragments, which was unexpected.

3. CONDENSED PHASE

Toshinori Suzuki (Kyoto University, Japan) began by providing a brief background on solvated electrons, proposing that they can be considered as radical anions in the condensed phase. Previously measured electron binding energies of the hydrated electron did not agree, spanning a range from 3.3 to 3.6 eV, with the discrepancies likely due to inelastic scattering effects in the liquids. To overcome complications involving inelastic scattering effects, they developed a spectral retrieval method that can retrieve the original kinetic energy distribution in the conduction band [Sci. Adv. 2019, 5, eaaw6896. DOI: 10.1126/sciadv.aaw6896]. Using a single order high-harmonic light source (\( \hbar \nu = 29 \text{ eV} \)), the electron binding energies have been resolved with near-perfect Gaussian distributions. The excited state lifetimes were also measured using a pump–probe setup.

4. PHOTODISSOCIATION

Hanna Reisler (University of Southern California, USA) presented work on the ultraviolet (UV) photodissociation of pyruvic acid, CH$_3$COCOOH, using time-of-flight mass spectrometry (TOFMS) and time-sliced velocity map imaging (VMI) at USC [J. Chem. Phys. 2013, 138, 144201. DOI: 10.1063/1.4798929] and a high-resolution time-resolved multiplexed photoionization mass spectrometer (MPIMS) at Sandia National Laboratories [Rev. Sci. Instrum. 2008, 79, 104103. DOI: 10.1063/1.3000004]. The dissociation from the S$_1$ electronic state (at 351 nm) yields CH$_3$COH fragments, acetaldehyde and vinyl alcohol. Dissociation from the S$_2$ electronic state (accessed through two photon excitation) and the S$_3$ state (reached by absorption of 193 nm light) yields H, OH, CH$_3$CO, HOCO, CH$_2$CO and CH$_3$ fragments. Three-body fragmentation processes with synchronous and sequential fragmentation mechanisms were discussed.

Kaijun Yuan (Dalian Institute of Chemical Physics, Chinese Academy of Science, China) presented recent work on the vacuum ultraviolet (VUV) photochemistry of water molecules at several wavelengths with the high resolution H-atom Rydberg tagging technique and a new VUV free-electron laser [Nat. Commun. 2019, 10, 1250. DOI: 10.1038/s41467-019-09176-z; J. Chem. Phys. 2018, 148, 124301. DOI: 10.1063/1.5022108]. Over the 115–140 nm wavelength range, OH radicals (in the \( \tilde{X} \) electronic state) were detected and observed to have high rotational energy. At wavelengths shorter than 115 nm, vibrationally and electronically excited “super rotor” OH radicals were observed (\( \tilde{X} \) and \( \tilde{A} \) electronic states). When H$_2$O molecules absorb photons around 112 nm, they are electronically excited to the \( \tilde{E} \) state, and highly vibrationally excited OH radical products are observed following relaxation. The OH super rotor products are stable by virtue of the associated centrifugal barriers. Below 107.5 nm, three body dissociation channels are dominant, giving O(\(^{1}\text{P}, ^{1}\text{D}) + 2\text{H} \), which may be responsible for the production of oxygen in Earth’s atmosphere.

Luis Bahares (Universidad Complutense de Madrid, Spain) discussed the photochemistry of the ethyl radical, CH$_3$CH$_2$ [Chem. Sci. 2019, 10, 6494. DOI: 10.1039/c9sc02140j]. Following excitation to the 3p Rydberg state, using a 2 + 1 ionization scheme, CH$_3$CH$_2$ radicals dissociated to give H atom photofragments that were detected by VMI. Photo-dissociation action spectra were recorded by monitoring the H atom photofragments as a function of wavelength. By repeating the experiments using various isotopologues of the ethyl radical, it is now understood that an \( \alpha \)-hydrogen is eliminated (CH$_3$CH$_2$* \( \rightarrow \) CH$_3$CH + H). Using high-level \textit{ab initio} electronic structure calculations of the potential energy curves and nonadiabatic coupling matrix elements, the H-elimination mechanism was elucidated. The initial ro-vibrational energy content of the radical nonadiabatically crosses into a valence bound state, which is then followed by dissociation through a CI.

5. ATMOSPHERIC CHEMISTRY

Dwayne Heard (University of Leeds, U.K.) discussed the atmospheric chemistry of free radicals in China, with particular focus on the OH radical. The OH radical plays an important role in the atmosphere; it can initiate the formation of a wide range of secondary products, which are implicated in poor air quality. Measurements of OH, HO$_2$, and RO$_2$ in Central Beijing (winter of 2016/2017 and summer 2017) and Tibet (2019), and HCHO additionally in Beijing, were obtained for the first time using a fluorescence assay by a gas expansion (FAGE) instrument, using 308 nm light. Fluorescence cells were used on the ground to detect OH, with the aim of understanding the processes leading to the frequent haze events in the winter and the high O$_3$ concentrations in the summer. By analyzing the measurements from Beijing during the winter haze events, photolysis of nitrous acid (HONO) is believed to be the dominant source of OH. During the summer, the processes are more complicated. By employing the Master Chemical Mechanism [Atmos. Chem. Phys. 2018, 18, 2547. DOI: 10.5194/acp-18-2547-2018], a Box Model is used to describe the radical initiated degradation of 140 volatile organic compounds (VOCs) through to CO$_2$ and H$_2$O. The measurements of OH were compared against the Box Model calculations, with agreement indicating that the processes are well understood. On the basis of the results, the model can accurately describe processes involving moderate NO$_2$ levels, but it is not as good for conditions of low or high NO$_2$ concentrations.

Christa Fitttschen (CNRS-Université de Lille, France) presented evidence that ROOOH may be a source of interference in FAGE instruments that results in the observation of an unexpectedly high OH radical concentration (compared to predictions from models) [Atmos. Chem. Phys. 2019, 19, 349. DOI: 10.5194/acp-19-349-2019]. ROOOH is the product of the reaction between RO$_2$ and OH radicals, a reaction that becomes especially important in areas with low NO concentrations [Chem. Phys. Lett. 2019, 725, 102. DOI: 10.1016/j.cplett.2019.04.002]. The experiments conducted employed a FAGE instrument coupled to laser photolysis, and time-resolved OH decays were recorded under different conditions. RO$_2$ radicals, generated by photolysis of a mixture of volatile organic compounds such as isoprene (C$_5$H$_{10}$) or methane (CH$_4$) with O$_3$/H$_2$O, can undergo self-reaction or react with OH to yield ROOOH. The OH decay recorded following the first laser shot signifies a decay in [OH] consistent with the OH + RH \( \rightarrow \) RO$_2$ mechanism. The OH concentration decay curve following the second laser shot suggests that a fraction of OH radicals react with RO$_2$: OH + RO$_2$ \( \rightarrow \) ROOOH, whose interference in the FAGE instrument leads to an increase in OH signal at long reaction time. It is
proposed that the presence of ROOOH, even in low concentrations (~100 ppt), may explain the interference in FAGE measurements when detecting the concentration of OH radicals.

Scott Kable (University of New South Wales, Australia) presented recent results demonstrating the oxidative loss of formaldehyde (CH\textsubscript{2}O), which was one of the first detected VOCs in the atmosphere. Using cavity ringdown spectroscopy (CRDS), spectra were recorded by monitoring the HO\textsubscript{2} product of the CH\textsubscript{2}O + O\textsubscript{2} reaction in a helium carrier gas. One surprise was the observation of HO\textsubscript{2} fragments following photoexcitation with energies lower than the dissociation threshold. For example, relaxation from the S\textsubscript{1} electronic state to the 4\textsuperscript{v} vibrational level of the ground state (S\textsubscript{0}), which lies 25 kJ/mol below the H + HCO dissociation limit, still results in formation of HO\textsubscript{2} fragments. The pressure dependence of the reaction indicates that the parent CH\textsubscript{2}O is reacting with O\textsubscript{2} in an unknown mechanism. Various possibilities were discussed, and these are the subject of ongoing experimental and computational research.

Jim Jr-Min Lin (Academia Sinica and National Taiwan University, Taiwan) provided a review on the structural dependence of the Criegee intermediates on their reactivity and also discussed the possible catalytic role of water in reactions involving Criegee intermediates [J. Phys. Chem. A 2017, 123, 8336. DOI: 10.1021/acs.jpca.9b07117]. The syn conformer of the CH\textsubscript{2}CHOO intermediate is known to thermally decompose to form OH and vinyloxy radicals, whereas the anti conformer reacts quickly with H\textsubscript{2}O. The syn-CH\textsubscript{2}CHOO + NH\textsubscript{3} reaction was investigated with and without H\textsubscript{2}O, and it was discussed that the NH\textsubscript{3} and H\textsubscript{2}O molecules cooperatively affect the reaction. Pseudo-first-order rate coefficients for the reactions were determined and compared against computational predictions of the energies and barriers along the reaction coordinates.

Jari Peltola (Eskola Group, University of Helsinki, Finland) presented studies of the temperature and pressure dependence on the kinetics of the decomposition of the CH\textsubscript{3}OO Criegee intermediate and the reaction of CH\textsubscript{3}OO with formic acid [Chem. Lett. 2019, 124, 465. DOI: 10.1021/acs.jpclett.9b00740] using the high-repetition-rate OH LIF method, through which the unimolecular reaction rate of the syn-CH\textsubscript{3}CHOO structure was measured. The findings suggested that unimolecular decomposition of the syn conformer is a major source of its consumption in the atmosphere.

6. SPECTROSCOPY AND DYNAMICS

Hongmei Su (Beijing Normal University, China) presented findings on the time-resolved UV−vis absorption spectroscopy of guanine (G), an important nucleobase in DNA oxidative damage and DNA charge transfer processes. DNA can be damaged by UV radiation and ionization, as well as by free radicals. By employing transient UV−vis spectroscopy, the one-electron oxidation of G, followed by deprotonation of the duplex, triplex, and quadruplex DNA, was directly monitored [J. Am. Chem. Soc. 2015, 137, 259. DOI: 10.1021/jacs.5b05285; J. Phys. Chem. B 2019, 123, 2853. DOI: 10.1021/acs.jpcb.9b00608]. The unique deprotonation pathway of the guanine radical cation (G\textsuperscript{••}) in the G-quadruplex was revealed, forming the N\textsubscript{7}−H deprotonated radical G(N\textsubscript{7}−H\textsuperscript{•}), which has a characteristic absorption band at 640 nm. The G\textsuperscript{••} deprotonation rate in the quadruplex was slower than in the duplex, suggesting the quadruplex structure may lead to less interruption in the hole transfer process in DNA. In addition, quantum chemical calculations were employed to predict how OH oxidizes guanine. Energy profiles for OH addition/elimination pathways were calculated using density functional theory (DFT), with the solvent effects simulated by the polarizable continuum model (PCM). The PCM calculations predicted the barrier to be high; however, the barrier was significantly reduced when explicit water molecules were considered as catalysts. This reaction occurs through a water-assisted H transfer process. Time-resolved IR spectra have captured the G\textsubscript{••}OH radical intermediate, which was identified through the support of harmonic vibrational frequency calculations, confirming that water can indeed act as a catalyst and OH addition reactions are more prominent than abstraction reactions.

Terry Miller (The Ohio State University, USA) presented calculations of vibronic eigenfunctions in the vicinity of CIs. Experimentally, CIs along reaction paths can be difficult to
measure and characterize; however, the Cls of Jahn–Teller (JT) active molecules can sometimes be much easier to study. Spectroscopic data can be used to compare against the results of calculated vibronic eigenvalues of JT active molecules, confirming the validity of the nonadiabatic calculations. For example, they showed that experimentally measured parameters describing the effects of dynamic molecular distortion on the rotational spectra of JT active molecules can be accurately predicted by calculations.

Neil Reilly (University of Massachusetts, USA) discussed spectroscopic data of a resonance-stabilized C2H radical formed in discharges of toluene and 1,6-heptadiyne. Hole-burning and two-color ion-yield measurements confirm that only one isomer, with an adiabatic excitation energy of 6.93 eV, contributes to the spectrum obtained using mass-selected resonant two-color-two-photon ionization. It was proposed that the C2H molecule contains a 1-vinylpropargyl (C3H4) chromophore because both species absorb in similar spectral regions [J. Am. Chem. Soc. 2009, 131, 13423. DOI: 10.1021/ja904521c]. Indeed, an ab initio calculation of the adiabatic ionization energy (AIE) of the 1-ethynylcyclopentenyl radical, which contains the trans-1-vinylpropargyl chromophore, agrees quantitatively with the experimentally measured value. This result, along with other spectroscopic arguments and chemical evidence, strongly suggests identification of the C2H species as the 1-ethynylcyclopent-2-enyl radical (1ecpr). Its detection in a toluene discharge suggests a connection to the complex regions [J. Am. Chem. Soc. 2009, 131, 13423. DOI: 10.1021/ja904521c].

Ge Sun (Zhang Group, University of California, Riverside, USA) delivered a talk about the photodissociation dynamics of the thiomethoxy radical (CH3S) via the B state. USA) delivered a talk about the photodissociation dynamics of the thiomethoxy radical (CH3S) via the B state. They showed that experimentally measured parameters describing the effects of dynamic molecular distortion on the rotational spectra of JT active molecules can be accurately predicted by calculations.

Gary Douterly (University of Georgia, USA) discussed the infrared (IR) spectra of the propyl radicals over the CH stretching region of the spectrum, as measured in superfluid helium nanodroplets and solid parahydrogen (p-H2) matrices. In the helium nanodroplet isolation (HENDI) technique, precursor molecules were pyrolyzed to produce propyl radicals, which were doped into the droplets and irradiated with a tunable IR optical parametric oscillator (OPO) laser [J. Chem. Phys. 2016, 145, 224304. DOI: 10.1063/1.4971239]. Using the p-H2 matrix isolation technique, the precursor molecules and p-H2 gas were simultaneously deposited onto the matrix. Then, photolysis was used to decompose the precursor into propyl radicals, and the IR spectra were collected using a Fourier-transform infrared (FTIR) spectrometer [J. Mol. Spectrosc. 2019, 363, 111170. DOI: 10.1016/j.jms.2019.07.001]. The resulting spectra were compared against high-level electronic structure calculations, and the observed spectral complexity was determined to originate from an extensive network of anharmonic resonance polyads.

Xiaoqing Zeng (Fudan University, China) discussed the gas-phase generation, spectroscopic characterization, and conformational properties of heterocumulenic radicals that contain the bent pseudohalogen NSO. By using high-vacuum flash pyrolysis (HVFP) of an oxathiazyne-like sulfinylnitrene (CF3S(O)N) at 600 °C, the pseudohalogen radical *NSO has been produced in the gas phase and subsequently characterized with FTIR spectroscopy in solid Ar and Ne matrices [Angew. Chem., Int. Ed. 2016, 55, 1507. DOI: 10.1002/anie.201510105]. By analogy, the HVFP of sulfinyl pseudohalides (CF3S(O)NCO and CF3S(O)NSO) in the gas phase yields the highly delocalized heterocumulenic radicals OSNCO* [Angew. Chem., Int. Ed. 2016, 55, 1507. DOI: 10.1002/anie.201611576] and OSNSO* [J. Am. Chem. Soc. 2018, 140, 1231. DOI: 10.1021/jacs.7b12622], respectively. In addition to the photoinduced interconversion of the anti and syn conformations observed in cryogenic Ar matrices, the low activation barriers for the out-of-plane rotation of the S–N bond in OSNCO* (0.33 ± 0.03 kcal/mol) and the in-plane N-inversion in OSNSO* (1.18 ± 0.07 kcal/mol) have been experimentally established.

Shuai-Ming Hu (University of Science and Technology of China, China) presented the recent observation of a Fano profile in the spectroscopic measurements of HD using cavity-enhanced absorption spectroscopy. The asymmetric Fano profile was considered as a result of the interference between a discrete ro-vibrational transition and a continuum, due to a far off-resonance electronic transition. The line centers of R(1) and R(3) around 1.39 μm in the first overtone band were determined with an accuracy of 0.24 MHz, which provides a strict test of quantum electrodynamics in a four-body system and paves the way for an independent determination of the proton-to-electron mass ratio. The asymmetrical Fano-type line profile can also be used to resolve the 10e discrepancy between two previous independent measurements [Phys. Rev. Lett. 2018, 120, 153001. DOI: 10.1103/PhysRev-
Jens-Uwe Grabow (Leibniz-Universität Hannover, Germany) described a recent high-resolution molecular beam spectroscopic study of the $^{173}$YbF molecule in the $\Sigma^+_\nu$ electronic state, with the aim to measure the $^2Q_{J\nu}$ parameters (corresponding to the molecular fine, magnetic hyperfine, and nuclear electric quadrupole moments) for the $^{173}$Yb ($I = 5/2$) element [Phys. Rev. A 2019, 100, 022516. DOI: 10.1103/PhysRevA.100.022516]. Hyperfine structure corresponding to the $N = 3 \rightarrow 4$ and $N = 4 \rightarrow 5$ rotational transitions were observed in spectra recorded using the separated field pump/probe microwave optical double resonance (PPMORDR) technique. Fourier transform microwave (FTMW) spectroscopy was used to record over the $N = 0 \rightarrow 1$ rotational transition. The measured fine and hyperfine structures can be compared against computational predictions and may be useful for the spectroscopic analysis of the $^{173}$YbOH molecule.

7. CHEMICAL KINETICS AND APPLICATIONS

Craig Taatjes (Sandia National Laboratories, USA) described how the MPIMS facilitates isomer-resolved identification of intermediates and products in reactions. The smallest alkyl peroxy radical (CH$_3$OO) can self-react to form methanol (CH$_3$OH); however, the reaction with OH is very fast and can compete in the troposphere. Major species identified in the CH$_3$OO + OH reaction include CH$_3$OH, H$_2$O$_2$, and CH$_3$O. Using isotopic labeling, the concentrations of the detected species were determined. At higher pressures, close to atmospheric (740 Torr), the trioxy intermediate (CH$_3$OOO) was observed in spectra recorded using the separated field pump/probe microwave optical double resonance (PPMORDR) technique. Fourier transform microwave (FTMW) spectroscopy was used to record over the $N = 0 \rightarrow 1$ rotational transition. The measured fine and hyperfine structures can be compared against computational predictions and may be useful for the spectroscopic analysis of the $^{173}$YbOH molecule.

Patrick Hemberger (Paul Scherrer Institute, Switzerland) presented an investigation of the catalytic fast pyrolysis mechanism of the lignin model compound guaiacol by combining a catalytic reactor with the photoelectron photoion coincidence (PEPICO) technique. Using the PEPICO setup, photoion mass-selected threshold photoelectron spectra (ms-TPES) can be obtained to isomer-selectively detect reactive intermediates in catalytic processes [Chimia 2018, 72, 227. DOI: 10.533/chimia.2018.227; Nat. Commun. 2017, 8, 15946. DOI: 10.1038/ncomms15946]. The fulvenone ketene (η-CH$_2$H=CH=O), was identified as the central reactive intermediate in the catalytic fast pyrolysis of guaiacol and had not been previously found in these processes. The reaction mechanism involving the fulvenone intermediate was established. The combination of a catalytic reactor with PEPICO has the potential to elucidate complex heterogeneous catalysis mechanisms.

8. SURFACES

Alec Wodike (Max Planck Institute for Biophysical Chemistry, University of Göttingen, Germany) discussed the dynamics of vibrational energy pooling of CO molecules adsorbed on the surface of an NaCl crystal [Science 2019, 363, 158. DOI: 10.1126/science.aav4278]. Spectra were recorded using a mid-IR emission spectrometer, with light detected by a superconducting nanowire single-photon detector (SNSPD). After the excitation of the CO molecules to the first vibrationally excited state ($v = 1$), IR emission from states up to $v = 27$ are observed. Monte Carlo simulations predict that a few CO molecules collect the vibrational energy at the expense of those up to eight lattice sites away by selective excitation of transverse phonons in NaCl. The interconversion of the CO molecules are observed. In the ground vibrational state and at low vibrational levels, the C$^=$O$^-$ dipole stabilizes the electrostatic bond where the C atom is oriented toward an Na$^+$ ion. At higher vibrational levels, the dipole moment reverses to C$^\delta$O$^{\delta -}$, such that the O atom is adjacent to the Na$^+$ ion. The two orientational isomers of CO on the NaCl crystal have similar stabilities due to the binding energy, which is predominantly influenced by the interaction of the molecule’s quadrupole moment with the electric field gradient near the Na$^+$ ion. The quantum dynamical processes in the condensed phase are tested by this system.

Mike Ashfold (University of Bristol, UK) provided an engaging review of the work done in the past 10–15 years on diamond formation, specifically through chemical vapor deposition (CVD) [J. Phys. Condens. Matter 2009, 21, 364201. DOI: 10.1088/0953-8984/21/36/364201]. One challenge in probing microwave activated CVD is the inhomogeneity of the reactor volume, specifically the large temperature gradients between the plasma core, the substrate, and the reactor walls—which are reflected in the local chemistry and gas-phase species concentrations. These variations can be resolved using spectroscopy, CRDS and optical emission spectroscopy provide quantitative column densities and insights into the spatial distributions of the species in the reactor that derive from the input gases, typically CH$_4$, H$_2$, and Ar. Appropriate modeling needs to recognize not just the temperature (and thus location) dependent chemistry but also the mass dependent thermodiffusion; heavy Ar and hydrocarbon species diffuse from the hot regions more efficiently than the light H$_2$ molecules. To maximize diamond formation, the temperature of the substrate and the...
concentrations of H atoms and CH$_3$ free radicals adjacent to the growing diamond surface need to be optimized. Quantum mechanical (QM) and QM-molecular mechanics (MM) calculations have proven useful in helping to understand deposition onto diamond surfaces. The combined use of spectroscopy, plasma modeling, and QM/MM calculations have led to a much better understanding of the reactions occurring on growing diamond surfaces.

Tetsuya Hama (Hokkaido University, Japan) began by proposing a provocative question: How do gaseous species evolve into ices or other solids? The question was followed by a description of the current understanding of surface processes on dust grains in the interstellar medium, with a particular focus on tunneling surface reactions. Tunneling surface reactions were explained to be efficient at low temperatures because volatile atoms can barrierlessly absorb onto the dust surface through van der Waals forces and long-range interactions. In the case of a benzene (C$_6$H$_6$) surface, it is predicted that H atoms add to an amorphous surface, but not to a crystalline surface [J. Phys. Chem. Lett. 2014, 5, 3843. DOI: 10.1021/jz5019948]. To help explain the H atom addition to a C$_6$H$_6$ monomer, activation energies were calculated using DFT.

9. CONCLUSION

We are grateful for the contributions and support of The Chinese Journal of Chemical Physics, The Journal of Physical Chemistry, Zhejiang Normal University, State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, National Natural Science Foundation of China, Edwards, Sky Technology Development, and Suzhou Huayang Science Vacuum Equipment Co., Ltd.

We also appreciate the session chairs, the speakers, and the poster presenters who shared their fantastic research, and all the other participants who engaged in thought-provoking scientific conversations. We extend additional gratitude to Astrid Bergeat, Floyd Davis, Dwayne Heard, and Gyorgy Lendvay for judging the excellent posters presented at the ISFR. Six total awards were granted for the posters, two of which were sponsored by The Journal of Physical Chemistry. These were granted to Gregory Pullen (Doublerby Group, University of Georgia) and Qian Wang (Zhou Group, Fudan University). Four poster awards were sponsored by The Chinese Journal of Chemical Physics and were given to Giel Muller (Bieske Group, University of Melbourne), Guoqiang Tang (van de Meerakker Group, Radboud University), Ye Xia (Su Group, Beijing Normal University), and Wei Zhang (Xia Group, Institute of Chemistry, Chinese Academy of Sciences).

The 36th International Symposium on Free Radicals will be held in 2021 at the AlbaNova University Centre of Stockholm University in Stockholm, Sweden. Richard Thomas (Stockholm University) will serve as the chair, and Åsa Larson, Wolf Geppert, and Mats Larsson will co-chair the conference. The tradition of excellence will continue.

Giel Muller  orcid.org/0000-0003-1173-6825
Gregory Pullen  orcid.org/0000-0002-8076-3053
Ge Sun

AUTHOR INFORMATION

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.jpca.9b11797

Notes
The authors declare no competing financial interest.