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SPECTROSCOPY AND REACTION DYNAMICS OF COLLISION COMPLEXES CONTAINING HYDROXYL RADICALS

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Abstract

The intermolecular bending and stretching vibrations supported by the OH ($X^2\Pi$) + Ar (1S_0) potential energy surfaces have been accessed by stimulated emission pumping (SEP) of the weakly bound OH-Ar ($X^2\Pi$) complex. Virtually all of the bound vibrational levels of the complex, from the zero-point level to the dissociation limit, have been identified. Since these vibrations sample a wide range of orientations and distances on the intermolecular potential energy surface, this data can now be used to derive a global potential energy surface for the OH ($X^2\Pi$) + Ar (1S_0) system. The first dissociation limit, producing OH ($X^2\Pi_{3/2}$) $v=0$, $j=3/2$ + Ar (1S_0) fragments, occurs between 93 and 103 cm^{-1} above the zero-point level as determined by the onset of bound-free features in the SEP spectra. In addition, metastable levels have been detected which lie as much as 200 cm^{-1} above the first dissociation limit. OH-Ar complexes prepared in these levels undergo predissociation by using OH rotational or spin-orbit excitation to break the weak OH-Ar intermolecular bond. Perturbation theory calculations have been carried out to understand the physical origin of the dynamical processes occurring on the OH ($X^2\Pi$) + Ar (1S_0) potential energy surfaces.

The experiments performed in this laboratory under DOE support aim to provide a detailed picture of the intermolecular potential between the open-shell hydroxyl radical and various collision partners. To date, our work has focused on the spectroscopic characterization of the interaction potential between the open-shell hydroxyl radical and an argon atom, and on the collision dynamics taking place on these potential energy surfaces [1-9]. These studies revealed an enormous change in the potential upon electronic excitation of the OH moiety: the binding energy of Ar to OH increases by nearly an order of magnitude, from approximate values of 90 to 740 cm^{-1} , and the OH (center-of-mass) to Ar separation distance decreases by 0.7 Å. The dramatic change in the potential is also manifested in the reaction dynamics: the rate of dissociation of the complex following vibrational excitation of OH occurs at least 10,000 times faster in the excited electronic state.

In the past year, we have implemented a new technique, stimulated emission pumping (SEP), to access the intermolecular stretching and bending vibrations supported by the OH ($X^2\Pi$) + Ar potentials [6-8]. Using theoretical calculations as a guide in understanding the energy level pattern [10,11], we have assigned the SEP spectrum. The lowest four levels are a manifold of bending levels ($v_b=0-3$) derived from the lowest rotational level of OH ($j=3/2$, $\omega=3/2$). These bends have average configurations ranging from the linear O-H-Ar (lowest energy state), through strongly bent, to linear H-O-Ar. The energy spread across the manifold of bending levels reflects the anisotropy of the intermolecular potential. The small splitting of the $v_b=2$ and $v_b=3$ levels shows the weak angular dependence of the potential in the region about the H-O-Ar orientation. At higher energies, the bending level pattern is repeated with one, two, and three quanta of intermolecular stretching excitation. The energy spread across the bending levels decreases with intermolecular stretching excitation, showing that the intermolecular potential becomes more isotropic as the average OH-Ar separation distance is increased. Another group of bending levels has been identified near 96 cm^{-1} , correlating to the rotationally excited $j=5/2$, $\omega=3/2$ level of OH. The first dissociation limit of OH-Ar $\rightarrow$ OH ($^2\Pi_{3/2}$) $v=0$, $j=3/2$ + Ar (1S_0) occurs within this manifold of bending levels. Using the lower limit $D_0 \geq 93 \text{ cm}^{-1}$ previously established by electronic

spectroscopy [5], we can now bracket the first dissociation limit between 93 and 103 cm^{-1} above the lowest OH-Ar level. A global potential energy surface for the OH ($X^2\Pi$) + Ar system is currently being derived based on the experimentally observed intermolecular vibrational energy levels from 0 - 89 cm^{-1} .

Using SEP, we have also accessed many predissociative resonances which lie as much as 200 cm^{-1} beyond the first dissociation limit [6,8]. OH-Ar complexes prepared in bending levels correlating with $j=5/2$, $\omega=3/2$ or higher rotational levels of OH, may predissociate by using OH rotational excitation to break the OH-Ar intermolecular bond. All of the OH-Ar levels which correlate with the spin-orbit excited state of OH $^2\Pi_{1/2}$ ($\omega=1/2$) lie above the first dissociation limit. Complexes prepared in $\omega=1/2$ states may predissociate via spin-orbit relaxation. Perturbation theory calculations have revealed the couplings responsible for these dynamical processes [7]. The rates of rotational and spin-orbit predissociation provide information on off-diagonal (anisotropic) terms in the interaction potential and the difference potential, respectively. The latter is the change in the intermolecular potential when the odd electron in the free radical lies in or out of the O-H-Ar plane. Perturbation theory calculations were also used to understand the large parity splitting in certain vibrational bands. The measured parity splitting was used to infer the magnitude of the difference potential ($\sim 12 \text{ cm}^{-1}$) in the region sampled by the first excited bend.

In the course of performing the SEP experiments, we discovered new information about the intermolecular vibrational levels supported by the electronically excited OH ($A^2\Sigma^+$) $v=0$ + Ar potential energy surface. We have recently identified the intermolecular bending vibration ($v_b'=1, v_s'=0$ or Π -bend), without stretching excitation, and the intermolecular bends with two quanta of excitation ($v_b'=2, v_s'=0$), denoted as the Σ and Δ bends [9]. Previous bound state calculations based on an *ab initio* potential energy surface [12] predicted an extremely high frequency bending vibration of $\sim 387 \text{ cm}^{-1}$ ($v_b'=1, v_s'=0$). In contrast, Bowman and coworkers [13] had deduced a bending vibrational frequency of 280.5 cm^{-1} based on their assignment of bend-stretch combination bands in the high energy region of the fluorescence excitation spectrum (features denoted as A, B, and C in Ref. 5 were assigned as $v_b'=1, v_s'=3-5$). Our observation of the fundamental bending vibration conclusively demonstrates that the OH ($A^2\Sigma^+$) + Ar potential in the region of the O-H-Ar attractive well is less anisotropic than predicted by the *ab initio* calculation [14]. Theoretical calculations are being performed in collaboration with D. C. Clary (Cambridge) to derive the OH ($A^2\Sigma^+$) + Ar potential energy surface based on our new experimental data.

In the past year, the personnel on this project have changed. Dr. Mary T. Berry, a postdoctoral associate, has become an Assistant Professor of Chemistry at the University of South Dakota. Mitchell R. Brustein obtained Ph.D. in 1991 based on this project with a thesis entitled "Spectroscopy and Dynamics of the OH-Ar van der Waals Complex." He is currently a postdoctoral associate at the University of Montreal. Two new graduate students are now working on this project: Richard A. Loomis, a third year student, and Leanna C. Giancarlo, a second year student.

The principal investigator, Marsha I. Lester, has devoted approximately 33% of her effort towards this project in the current term and expects to devote the same effort for the duration of the project.

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