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Femtosecond photoassociation spectroscopy: coherent bond formation

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Abstract

The method femtosecond photoassociation spectroscopy (FPAS) is introduced and we report on its application to the study of the reaction $Hg + Hg + h\nu \rightarrow Hg_2$. Our results demonstrate coherent bond formation obtained in the femtosecond time scale from free unbound reactants. The product Hg_2 is formed in the $D1_u$ state and shows a high degree of rotational anisotropy induced by the polarization of the binding femtosecond pulse.

1. Introduction

The two most fundamental processes of chemical reactions, bond formation and bond dissociation, have traditionally been studied by techniques which provide detailed information only about the initial and final stages of the reaction, leaving the intermediate steps to inference. These processes are very fast $(10^{-12}-10^{-14}$ s) and only recently have time resolved methods been able to directly capture the transition state dynamics [1]. Bond-breaking studies have had two critical advantages, the first of which is that the initial impact parameter and molecular orientation are well defined. Secondly, the photodissociation event may be triggered by an ultrafast laser pulse, thus providing a 'time zero' for the initiation of the reaction. Using femtosecond techniques one is therefore able to interrogate the transition states of reactions in progress [2,3]. Bond formation, on the other hand, is challenging because collisions occur at random times and with random impact parameters and because the short duration of the laser pulse

implies a concomitant loss in the number of atoms or molecules in close proximity.

Recently, van der Waals complexes have been introduced to restrict the reagent geometry and to allow the definition of a time zero for bimolecular reactions. These experiments by the groups of Zewail, Wittig and others use precursors which undergo a full collision reaction upon liberation of one of the reactants in the complex [4]. Femtosecond probing and control of a bimolecular reaction without precursors has been achieved in a pioneering experiment by Zewail and co-workers who introduced time zero of the gas phase collision for the reaction of Xe atoms with I_2 to produce XeI [5]. The Xe and I_2 have random distributions and are mostly unbound at room temperature. The femtosecond resolution defines the configuration space and offers sufficient sensitivity even though the number of atoms in close proximity is relatively small.

The photoassociation process, whereby a photon excites a free-to-bound transition, has been applied to the spectroscopic study of excimer and exciplex
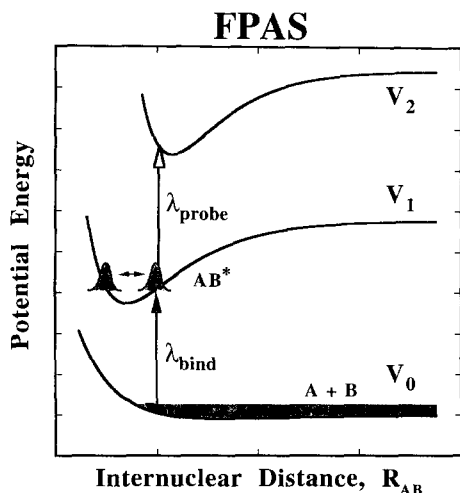
FPAS

Fig. 1. General scheme for femtosecond photoassociation spectroscopy (FPAS) of a gas-phase system having a repulsive ground state V_0. Binding by the laser is followed by excitation to a higher state V_2; the evolution of the wavepacket along V_1 is probed by varying the delay between λ_{bind} and λ_{probe} and monitoring the fluorescence from V_2 or the depletion of the fluorescence from V_1.

molecules [6–8] including those formed from laser cooled atoms [9,10]. Setser and co-workers have studied gas phase laser assisted reactions based on this principle [11,12]. Their experiments involve two-photon (nanosecond) excitation of a halogen containing compound RX in the presence of Xe to form the charge-transfer complex $Xe^+:RX^-$, which then dissociates into XeX^* and R.

In this Letter, we present a method devised specifically to study the dynamics of bond formation in real time. The method, femtosecond photoassociation spectroscopy (FPAS), schematically represented in Fig. 1, uses femtosecond pulses to trigger coherent chemical bonding between free, randomly distributed reactants. Here we describe reactions of the type:

$$A + B + h\nu \rightarrow AB. \qquad (1)$$

A 'binding' femtosecond laser pulse λ_{bind} causes chemical bond formation between a small number of reactant pairs which at the time of the laser pulse have an internuclear separation defined by $\Delta R_x = R_{max} - R_{min}$, but are not bound. In the simple case of diatomic bond formation ΔR_x is found by taking the difference between the excited state potential $V_1(R)$, and the sum of the ground state potential $V_0(R)$ and the available energy ($E_{avail} = E_{binding} + E_{thermal}$). This

helps to determine the Franck–Condon region for the free–bound transition. With the bond formation a wave packet is born in the new molecular state and its temporal evolution may be monitored by a second femtosecond pulse of wavelength λ_{probe}. In addition to selecting the initial internuclear separation, λ_{bind} restricts the orientation of bond formation because the atoms must be favorably aligned with respect to the polarization vector of the laser. This makes it possible to obtain time resolved rotational information about the newly formed species. The probing pulse, tuned to an electronic transition with significantly restrictive Franck–Condon factor, achieves discrimination of interatomic motion of the product molecule. The results from this technique thus contain vibrational and rotational coherence information and may be used to fully characterize the transient species in a way that is analogous to femtosecond bound to bound state experiments [13,14].

The specific system we have examined is

$$Hg + Hg + h\nu \rightarrow Hg_2^*. \qquad (2)$$

The formation of the excimer Hg_2^* following optical excitation of mercury vapor has been observed since the early 1900s by Rayleigh, among others [15,16]. In the 1970s interest in its spectroscopy was sparked by the search for a tunable high gain laser medium (see, for example, Ref. [17]). The excimer of mercury has been considered to be ideal for this purpose because the repulsive ground state ensures population inversion. More recent spectroscopic studies have taken advantage of two color laser spectroscopy [18,19] and supersonic jet expansion techniques [20–22] to obtain highly detailed spectroscopic information about the electronic states of Hg_2.

2. Experimental

The femtosecond laser system used for these experiments is a home built CPM pulsed dye-amplified system, which can provide 50 fs pulses at 624 nm with an energy of 0.5 mJ per pulse. The laser output was split into two arms of a Mach-Zhender interferometer. One arm was doubled with a 0.1 mm KDP crystal and then the two beams were recombined collinearly using a dichroic beam splitter. A calcite Glan-Laser linear polarizer and an achromatic 400–

700 nm half wavelength plate were used to ensure high polarization ratios of pump and probe beams. Rotation of the $\lambda/2$ plate controlled the orientation of the polarization vector of the probe beam without a measurable effect on temporal delay. Care was taken in the selection of optics and SHG crystal to preserve the short temporal duration of our pulses. Binding (312 nm) and probe (624 nm) lasers were focused in the mercury cell by a 200 mm lens and laser induced fluorescence (LIF) was collected perpendicular to the lasers through a 0.27 m spectrometer.

The signal obtained at each time delay between the binding and probe pulses was averaged for 10 laser shots. Typical transients contained data from 200 different time delays and were averages of 50 scans. The sample, triply vacuum distilled and certified to contain a total of less than one part per million impurities (Bethlehem Apparatus Co.), was introduced to a thoroughly cleaned and vacuum baked glass line by injection over an argon atmosphere. The injection port was sealed and the sample pumped to 10^{-5} Torr. A portion of the line containing the quartz cell and a 'U' trap was then closed to the rest of the pumping station and immersed in liquid nitrogen to achieve cryopumping while the cell was sealed off.

We checked the purity of the sample by LIF in the 190–850 nm region at high laser intensity. Fluorescence from the cell showed two Hg_2 bands and some atomic mercury lines (resulting from multiphoton excitation); we found no spectral evidence of contamination in the sample. The bulb was wrapped in heating tape and maintained at a constant temperature throughout the experiment. Most of our results were obtained at 160°C, which corresponds to 4.2 Torr [23].

3. Results and discussion

The potential energy curves of the electronic states relevant to our experiment are shown in Fig. 2. The ground state potential $X0_g^+$ is taken from Koperski et al. [22], who determined the depth D_e of the van der Waals well in the ground state in jet-cooled Hg_2 to be 380 ± 15 cm^{-1}, see Fig. 2 (insert). The $D1_u$ state, well known in absorption and emission because it is
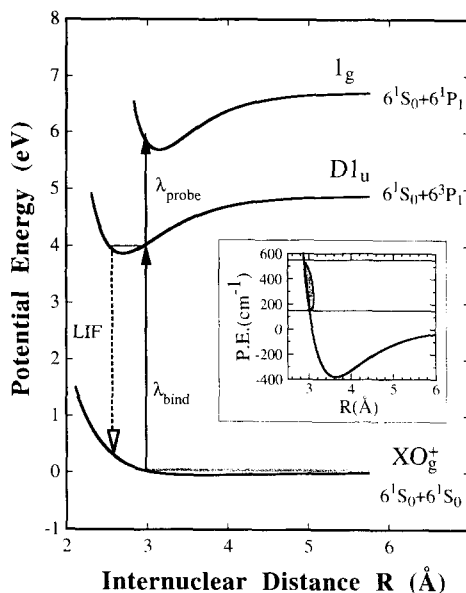

Fig. 2. FPAS experiment on mercury. The initial (binding) pulse forms Hg_2 in the $D1_u$ state; we monitor the depletion of the $D1_u \rightarrow X0_g^+$ fluorescence as λ_{probe} causes excitation to the 1_g state (see text). The region of most probable excitation from the ground state is shown in the insert. The lines at 150 and 550 cm^{-1} above the $X0_g^+$ state delineate the most probable kinetic energies of the atoms, given a thermal distribution at $T = 160$°C.

the first ungerade state optically accessible from the ground state, has been studied in jet cooled Hg_2. We assumed a Morse potential and used the parameters D_e, ω_e and $\omega_e x_e$ of Zhenacker et al. [20]. T_e and R_e were determined by finding the best correlation to the 6^3P_1 atomic energy level and the 335 nm emission from the bottom of the $D1_u$ state to the $X0^+g$ state [18,19]. The upper state reached by one probe laser photon is the 1_g state, which correlates with Hg $6^1P_1 + 6^1S_0$ [24,25]. We have sketched the 1_g potential curve based on the Morse parameters from published figures. Also shown is the region ΔR_x of most probable excitation based on the average thermal energy kT of the atoms and the spectrum of our binding pulse. Notice that the narrow range of interatomic distances captured by the excitation process is in the repulsive part of the ground state potential, above the dissociation energy of the dimer.

Fig. 3 shows the FPAS transients obtained following binding excitation at 312 nm and probing at 624 nm. The LIF signal from the $D1_u \rightarrow X0_g^+$ transition

at 340 nm was detected selectively with a spectrometer having 10 nm spectral acceptance. For negative time delays (probe before binding pulse) the LIF intensity is higher than for positive time delays. This is because the probe pulse excites the molecules to a higher electronic state, thus depleting the $D1_u$ population. Note the rapid onset of depletion (within the duration of the pulse) which indicates that photoassociation occurs only in the presence of the binding laser.

The FPAS signal from the nascent Hg_2^* exhibits rotational anisotropy, which is caused by preferential absorption by atom-pairs aligned with the polarization vector of the binding laser (parallel transition). This coherence dephases because of the large distribution of angular momenta of the nascent molecules. In light of work by Zewail and Felker we expect to observe full rephasing after a time $t = l/2B$, where B is the rotational constant of the $D1_u$ state and l is an integer [26–29]. A detailed study of the nascent rotational distribution and dephasing will be reported elsewhere [30]; these experiments will be performed on monoisotopic mercury to further simplify the

Fig. 4. Rotational anisotropy $r(t)$ from the FPAS transients shown in Fig. 3. The points are the experimentally determined values; the line represents a least-squares fit to the data (see text).
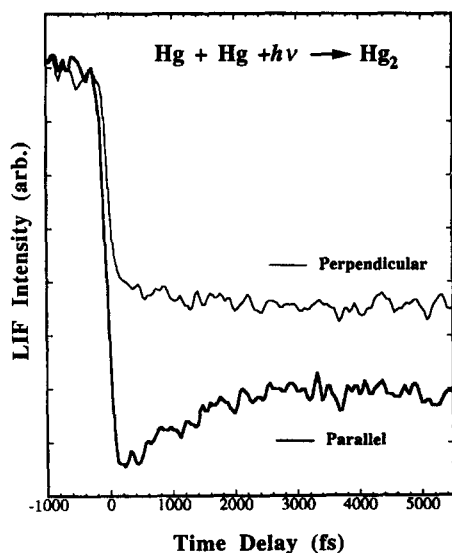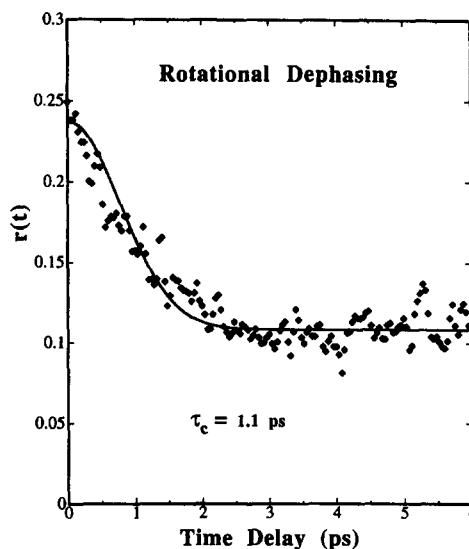

Fig. 3. FPAS transients showing depletion of the $D1_u \rightarrow X0_g^+$ fluorescence as shown in Fig. 2. Data is for the binding and probe lasers polarized parallel or perpendicular to one another. Note the rotational dephasing of the initial anisotropy (see text).

observed dynamics. Comparison of transients obtained when binding and probe lasers were polarized parallel to each other to those obtained when they were perpendicular allows us to separate rotational and vibrational dynamics.

The purely rotational component (anisotropy) is obtained by the weighted difference

$$r(t) = \frac{I_\| - I_\perp}{I_\| + 2I_\perp}, \tag{3}$$

where $I_\|$ and $I_\perp$ represent parallel and perpendicular bind–probe transients, respectively. Fig. 4 shows the rotational dephasing of the FPAS results presented in Fig. 3. Based on a simple model which treats the rotational population as a Gaussian centered about $j = 0$, an expression for $r(t)$ can be obtained [28,29],

$$r(t) = 0.1 + 0.3\exp\left[-(t/\tau_c)^2\right], \tag{4}$$

where $\tau_c = (\Delta j\omega)^{-1}$ is defined as the dephasing time for molecules with a rotational distribution characterized by a half-width at $1/e$ of Δj and a rotational frequency $\omega = 4\pi B$. Non-linear least-squares fitting of the experimental $r(t)$ give the best agreement with the data when $\tau_c = 1.1$ ps, corre-

sponding to $\Delta j = 110$. We are developing a theoretical framework to determine the j population that results from the photoassociation process and to study its time evolution. This model will help us to determine why the measured anisotropy is half of the theoretical maximum $r(t)_{t=0} = 0.4$.

In interpreting the data we have considered mechanisms other than photoassociation that may result in the formation of Hg_2^*. Some of the most likely alternatives we have explored are: (i) excitation of an equilibrium population of Hg_2 molecules, (ii) photolysis of an equilibrium population of Hg_3 molecules and (iii) excitation of an atomic transition followed by collisional association with another atom.

We have calculated that the ratio of dimers to monomers at our temperature and pressure is 3.5×10^{-5} [31]. While this is still a significant number, the Franck–Condon factor for a transition between the $X0_g^+$ and the $D1_u$ state is very unfavorable, see Fig. 2 (insert). The optical coupling region for λ_{bind} is ≈ 300 cm^{-1} above the dissociation energy of the dimer and at an internuclear distance that is 0.6 Å smaller than the ground state R_e. As an additional check, we nevertheless attempted to fit the experimental anisotropy to a thermal distribution of Hg dimers and found no correlation with our data.

At the temperature and pressure of the experiments the equilibrium concentration of trimers in the sample is much less than one in 10^{15}, which we consider to be negligible. Furthermore, photolysis of a trimer with the characteristics of Hg_3 would have resulted in very different dynamics to those observed (see for example the photodissociation dynamics of HgI_2 in Ref. [32]).

The formation of Hg_2^* by collisional association of excited and ground state mercury atoms is an important source of short lived ($\tau < 50$ ns) excimers [33] [1]. However, it should be pointed out that this does not affect the FPAS data for three reasons. First, the excited mercury atoms would not retain the anisotropy caused by the polarized laser beams. Second, the mean time between collisions under these conditions is three to four orders of magnitude slower

than our femtosecond–picosecond experiment. Third, a three body collision would be required to form a bound molecule by this pathway and these are much less probable than two body collisions. We chose LIF-depletion probing for this experiment to isolate the FPAS signal; photoassociation occurs only during the binding pulse (≈ 100 fs) and the probe serves as a time gate which monitors the bond formation dynamics on a time scale much shorter than collisional association (> 1 ns). The relative orientation between the polarization vectors of binding and probe lasers results in rotational anisotropy, which further distinguishes the FPAS signal from that of collisionally associated molecules.

Based on these considerations we have concluded that photoassociation is the only pathway consistent with the probe depletion data. Additionally, several 'check-type' experiments performed on the system have supported our conclusions. These include laser-intensity dependence of the signal, which was found to be linear with the binding pulse. This confirms that the fluorescence is caused by a single-photon excitation to the $D1_u$ state of the excimer. Increasing the laser intensity beyond a certain threshold value, however, caused a loss of signal as competing multiphoton processes became more important. Temperature/density dependence of the signal was also checked, and the observed trends were as expected (vide infra), for temperatures up to 400°C.

The magnitude of the FPAS signal depends critically on the number of atoms that have a neighbor within the distance ΔR_x at the time the femtosecond binding pulse is present. We start by using a radial distribution function to calculate the probability that a shell of radius r and thickness dr centered on a single atom contains a neighbor atom. We then integrate within the distance $\Delta R_x = R_{max} - R_{min}$, thus describing a 'reactive shell' using

$$P(r) = \int_{R_{min}}^{R_{max}} \rho g(r) 4\pi r^2 dr, \qquad (5)$$

where ρ is the number of atoms per unit volume (10^{17} cm^{-3} at $T = 433$ K) and $g(r)$ is the radial distribution function [31]. As a first approximation we used

$$g(r) = \exp[-V(r)/kT], \qquad (6)$$

[1] Callear and co-workers have published several studies on the spectroscopy of Hg_2 formed by collisional association. See Ref. [34].

where $V(r)$ is the potential energy between the atoms and $P(r)$ is the fraction of mercury atoms having a neighbor within the volume defined by ΔR_x. Using values consistent with our experimental conditions and the ground state potential from Koperski et al. [22], we calculate $P(r) \approx 7 \times 10^{-7}$. We have used $R_{min} = 2.98$ Å and $R_{max} = 3.07$ Å based on vertical transitions between the repulsive $X0_g^+$ state and the $D1_u$ state, taking into account the spectrum of the pulse and the available kinetic energy (see Fig. 2). Orientation and thermal energy distributions of each pair further reduce this number by one order of magnitude. On average, seven out of every 10^8 Hg atoms are bound by the laser; under the conditions of our experiments 10^5 mercury pairs are formed per pulse. We discriminate other sources of LIF by depletion-probing of the 335 nm $D1_u \rightarrow X0_g^+$ fluorescence.

In conclusion, we have introduced the FPAS method and demonstrated its usefulness for the study of time resolved chemical bond formation. We confirm the coherent photoassociation step by the anisotropy in our data, the linear dependence with laser intensity and the known spectroscopy of the system. Further studies will include tuning of the binding and probe lasers in order to observe vibrational coherence in the bond formation process more clearly. We plan to expand the FPAS method to the study of other reactions.

Acknowledgements

References

[1] J.C. Polanyi and A.H. Zewail, Accounts Chem. Res. 28 (1995) 119.

[2] A.H. Zewail, Femtochemistry: ultrafast dynamics of the chemical bond (World Scientific, Singapore, 1994).

[3] M. Dantus and G. Roberts, Comments At. Mol. Phys. 26 (1991) 131.

[4] J. Manz and L. Wöste, eds., Femtosecond chemistry, Vols. 1 and 2 (VCH Publishers, Weinheim, 1995).

[5] E.D. Potter, J.L. Herek, S. Pedersen, Q. Liu and A.H. Zewail, Nature 355 (1992) 66.

[6] H. Scheingraber and C.R. Vidal, J. Chem. Phys. 66 (1977) 3694.

[7] H.P. Grieneisen, K. Hohla and K.L. Kompa, Opt. Commun. 37 (1981) 97.

[8] D.J. Ehrlich and R.M. Osgood Jr., Phys. Rev. Letters 41 (1978) 547.

[9] H.R. Thorsheim, J. Weiner and P.S. Julienne, Phys. Rev. Letters 58 (1987) 2420.

[10] D. Kleppner, Phys. Today July (1995) 11.

[11] F. Huang, D.W. Setser and B.S. Cheong, Israel J. Chem. 34 (1994) 127, and references therein.

[12] T.O. Nelson, D.W. Setser and J. Qin, J. Phys. Chem. 97 (1993) 2585.

[13] M. Dantus, R.M. Bowman and A.H. Zewail, Nature 343 (1990) 737.

[14] M. Gruebele and A.H. Zewail, J. Chem. Phys. 98 (1993) 883.

[15] Lord Rayleigh, Proc. Roy. Soc. A 114 (1927) 620.

[16] R.W. Wood, Physical optics (Dover, New York, 1961) p. 636.

[17] E.W. Smith, R.E. Drullinger, M.M. Hessel and J. Cooper, J. Chem. Phys. 66 (1977) 5667.

[18] M. Stock, E.W. Smith, R.E. Drullinger and M.M. Hessel, J. Chem. Phys. 67 (1977) 2463.

[19] W. Kedzierski, J. Supranowicz, A. Czajkowski, M.J. Hinek, J.B. Atkinson and L. Krause, Chem. Phys. Letters 218 (1994) 314.

[20] A. Zehnacker, M.C. Duval, C. Jouvet, C. Ladeux-Dedonder, D. Solgadi, B. Soep and O. Bonoist d'Azy, J. Chem. Phys. 86 (1987) 6565.

[21] R.D. Van Zee, S.C. Blankespoor and T.S. Zwier, J. Chem. Phys. 88 (1988) 4650.

[22] J. Koperski, J.B. Atkinson and L. Krause, Chem. Phys. Letters 219 (1994) 161.

[23] D.R. Lide, ed., CRC handbook of chemistry and physics, 74th Ed. (CRC Press, Boca Raton, 1993).

[24] P.J. Hay and T.H. Dunning Jr., J. Chem. Phys. 65 (1976) 2679.

[25] F.H. Mies, W.J. Stevens and M. Krauss, J. Mol. Spectry. 72 (1978) 303.

[26] P.M. Felker and A.H. Zewail, J. Chem. Phys. 86 (1987) 2460.

[27] P.M. Felker, J. Phys. Chem. 96 (1992) 7844, and references therein.

[28] M. Dantus, R.M. Bowman, J.S. Baskin and A.H. Zewail, Chem. Phys. Letters 159 (1989) 406.

[29] J.S. Baskin and A.H. Zewail, J. Phys. Chem. 98 (1994) 3337.

[30] U. Marvet and M. Dantus, unpublished results.

[31] D.A. McQuarrie, Statistical mechanics (Harper and Row, New York, 1976) p. 144.

[32] M. Dantus, R.M. Bowman, M. Gruebele and A.H. Zewail, J. Chem. Phys. 91 (1989) 7437.

[33] H. Kuhn and K. Freudenberg, Z. Physik 76 (1932) 38.

[34] A.B. Callear and K.-L. Lai, Chem. Phys. 69 (1982) 1, and references therein.