

Ultraviolet Spectroscopy and UV Lasers

edited by

Prabhakar Misra

*Howard University
Washington, D.C.*

Mark A. Dubinskii

*Magnon, Inc.
Reisterstown, Maryland*



MARCEL DEKKER, INC.

NEW YORK · BA SEL

Copyright © 2001 by Marcel Dekker, Inc. All Rights Reserved.

MARCEL DEKKER, INC.



Register now on dekker.com and receive a discount coupon towards your next Dekker purchase. Registered users enjoy these advantages:

- ✓ Preview content online for free
- ✓ Quickly access your subscriptions and downloads
- ✓ Sign up for email notifications about new products and special offers in your subject of interest

Send your book order to your regular book supplier or directly to your nearest Marcel Dekker, Inc. office:

USA, Canada, South America:

5

Ways to Order

- 🌐 **Website:** www.dekker.com
- ☎ **Toll-free:** 1-800-228-1160
- 📠 **Fax:** 1-845-796-1772
- @ **E-mail:** bookorders@dekker.com
- ✉ **Mail:** Marcel Dekker, Inc., Cimarron Road
P.O. Box 5005, Monticello, NY 12701-5185

Europe, Africa, Middle East Far East, Australia, India, China:

5

Ways to Order

- 🌐 **Website:** www.dekker.com
- ☎ **Phone:** +41-061-260-6300
- 📠 **Fax:** +41-061-260-6333
- @ **E-mail:** intlorders@dekker.com
- ✉ **Mail:** Marcel Dekker, AG
Hutgasse 4, Postfach 812
CH-4001 Basel, Switzerland

Please include quantity, ISBN, author, title, shipping and billing addresses, telephone number/fax number/e-mail address, method of shipment, and purchase order numbers or credit card information.

To purchase offprints of chapters that appear in any Marcel Dekker, Inc. book or reprints of articles that appear in any Marcel Dekker, Inc. journal:
offprints@dekker.com

To inquire about special sales and bulk purchases of Marcel Dekker, Inc. books or journals:
bulksale@dekker.com

research + dekker.com → results

6

Spectroscopy and Applications of Diatomic and Triatomic Molecules Assisted by Laser Light at 157.6 nm

Alciviadis-Constantinos Cefalas and Evangelia Sarantopoulou

*National Hellenic Research Foundation, Theoretical and Physical
Chemistry Institute, Athens, Greece*

I. THE MOLECULAR FLUORINE LASER

Laser radiation from molecular fluorine transitions at 156.71, 157.48, and 157.59 nm was observed for the first time in 1978 by J. R. Woodworth and J. K. Rice [1,2]. They used e-beam excitation to achieve population inversion in a mixture of He (1500 mbar) and F₂ (5.3 mbar). The observed stimulated emission was assigned to the $^3\Pi_g \rightarrow ^3\Pi_u$ transitions of the F₂ molecule. The intensity of the laser pulse was 7 MW/cm² and the efficiency was 3.5%. The experimental setup used by Woodworth et al. was complicated and the system had to be pumped and filled back after each shot. Plummer et al. [3] in 1979 used a different more convenient technique by pumping mixtures of F₂ and He in a fast ultraviolet (UV)-preionized discharge. This technique proved successful for pumping of the excimer lasers and it was more flexible. The cathode electrode whose position was fixed consisted of a stainless steel mesh. The discharge volume could be varied by moving one electrode in order to find the optimum electrode spacing for higher laser output. In 1985 Cefalas et al. [4] developed a simple UV preionized F₂ laser of the fast-discharge type to measure the small signal gain by the passive cell absorption method. The gain with this equipment at optimum working conditions of 2 atm total gas pressure and 2 cm electrode spacing was found

to be $3.2\% \text{ cm}^{-1}$. The output energy was measured as 12 mJ per pulse and the pulse duration was 10 ns despite the use of gases with high concentration of impurities (0.1% impurities). With this experimental apparatus it was proved that the molecular fluorine laser had the potential to be a powerful VUV laser similar to the excimer lasers. Following its development, higher output energy of 15 mJ per pulse was achieved by Ishchenko et al. [5]. The above values of output energies were half those predicted by the theoretical calculations of Ohwa and Obara [6], if one considers only the dissociative collision of F_2 molecules by ion-ion recombination of energy transfer reaction and neglecting the direct excitation of F_2 molecules by electron impact or energy transfer from He^* -, He^{*-} -, and He_2^* -excited atoms or clusters.

The predictions of Ohwa and Obara were confirmed by Yamada et al. [7], who developed an F_2 laser that delivered 112 mJ per pulse at 8 atm total gas pressure. The electric circuit in this apparatus was similar to that developed by Cefalas et al. (1985) of the fast charge transfer type with UV preionization. The innovating point in the geometry of this cavity was the small distance between the electrodes of 10 mm, providing stable discharge even at higher gas pressure and hence improving the laser's performance. In an effort to investigate the physical parameters and limits of the F_2 molecular laser, Cefalas et al. used two discharge laser heads driven by a spark-gap switch to measure the small-signal gain and the saturation intensity in the oscillator–amplifier configuration [8,9]. The small-signal gain coefficient was measured to be $5.2 \pm 0.4\% \text{ cm}^{-1}$ at 3 atm total pressure and 1.5 cm electrode spacing. It was $4.1 \pm 0.4\% \text{ cm}^{-1}$ at 2 atm total pressure and 2 cm electrode spacing. The values of saturation intensities were found to be 5 MW/cm^2 and 4.6 MW/cm^2 , respectively. The dependences of the energy output and efficiency of the F_2 laser on the pump power (up to 40 MW/cm^3) have been studied by Kuznetsor and Sulakshin [10]. The maximum lasing efficiency was 0.05% and the laser radiation energy was 120 mJ at pressure of the He-F_2 mixture of 3 atm. A theoretical kinetics model successfully described the characteristics of the F_2 laser output. The authors concluded that at high gas pressure operation, where dissociation of the F_2 (A') state is accelerated, higher discharge pumping power is achieved [11]. The small-signal gain and the saturation intensity of the discharge pumped F_2 laser, operated at higher pressures (<10 atm) and higher excitation rates ($7\text{--}39 \text{ MW/cm}^3$), were measured [12] with a similar oscillator–amplifier configuration to that used by Cefalas et al. [8,9]. The small-signal net gain with this apparatus now reaches $37 \pm 4\% \text{ cm}^{-1}$ at an excitation rate of approximately 26 MW/cm^3 for a 6-atm gas pressure. The saturation intensity, which depends on a nonsaturation absorption coefficient, was estimated. The output energy and the temporal behavior of a molecular F_2^* laser pumped by a coaxial electron beam have been measured in gas mixtures of He/F_2 and He/Ne/F_2 [13]. The highest output energy of 172 mJ has been obtained in a mixture of He/Ne/F_2 (19.9%/80%/0.1%) at a pressure of 12 bar, correspond-

ing to a specific output energy of 10.8 Joule/lit and an intrinsic efficiency of 2.6%. An electron beam pumped molecular F_2^* laser with pulse width up to 160 ns, and output energy of 1.7 J (optical flux of 4.6 MW/cm²) has been realized [14] by the same group. The widths of the laser pulses seem to be limited by the duration of the excitation pulse (160 ns). For specific output powers up to 100 kW/cm³, no signs of self-terminating laser pulses, due to bottlenecking in the lower laser level, have been observed. The application of a prepulse–main pulse excitation scheme utilizing a saturable magnetic switch in combination with x-ray preionization has resulted in the generation of long optical pulses from a molecular fluorine laser [15]. Optimum laser pulse durations of 70 ns (full width at half maximum) have been obtained in a gas mixture of helium and 3 mbar fluorine at a total pressure of 2 bar. Laser pulse duration was limited by instabilities in the electric discharge. The laser pulse duration was found to decrease with increasing fluorine pressure and to saturate with increasing current density.

II. PHOTOLITHOGRAPHY AT 157 nm

Despite the fact that the molecular fluorine laser emits strong monochromatic radiation at 157.6, its nontunability in the VUV is a serious drawback for a wide range of applications. However, this disadvantage is balanced by the high energy emitted per photon. The molecular fluorine laser has the potential to be used in the near future in many areas of science and technology. Indeed, next-generation microelectronics circuits will have minimum dimensions below 100 nm. It is envisioned that 157 nm laser lithography will be the next step in optical lithography. At 157 nm, under VUV illumination of the mask target, lithographic features with dimensions of 0.10 μm on the photoresist have been achieved by an F_2 laser lithographic stepper developed by Exitech UK [16]. The high-repetition-rate molecular fluorine laser developed by Lambda Physik in Germany was likewise the driving force for developing 157 nm photolithography. The first to propose the F_2 laser in photolithography was White et al. in 1984 [17]. A 2 kHz repetition rate discharge-pumped molecular fluorine laser oscillating at 157 nm was developed. It has achieved an average power of 22 W at the repetition rate of 2 kHz with a newly developed solid-state pulse power module with 6 J/pulse input energy [18]. Single-line operation at 157.6 nm was achieved by means of a prism assembly. Laser operation at repetition rates up to 1 kHz without signs of power saturation results in an average power of 15 W. The energy stability with these devices was comparable to the stability of the ArF laser [19].

Research in new photoresists for 157 nm photolithography [20–26] requires the investigation of basic optical and photochemical studies at these wavelengths. The high value of the absorption coefficient of the polymeric materials in the VUV, from 10^4 to 10^6 cm⁻¹, imposes restrictions on selection of the pho-

toresists for 157 nm photolithography, demanding high-purity materials and defect-free thin films. There is a complete bond breaking of all the organic molecules at these wavelengths. The parent molecule disintegrates into small fragments, atomic, diatomic or triatomic, which fly apart with supersonic speeds. This occurs because, for all the organic molecules, the dissociative excited states of the small radicals occupy the energy range above 6.2 eV (200 nm). Therefore the photodissociation process could impose serious problems on the optics of the projection system by contaminating it.

To overcome this serious problem, complete microscopic description of the photodissociation dynamics involved in the scission of the polymer chains, and the dynamics of the extraction of the photoproducts, is required at 157 nm. Until now various theories have been developed that analyze the role of the excited species in ultraviolet laser materials ablation. The complexity and diversity of the processes involved in laser ablation dynamics, such as laser excitation of the absorbing molecules and energy transfer from the excited parent molecules into the internal and the translational degrees of freedom of the photofragments, require for their description the analytical expression of the potential energy surfaces of the parent molecules and the photofragments, for both ground and the excited states [27].

As the first contribution in this subject, and in order to investigate basic photochemical mechanisms of the photodissociation dynamics of various polymeric materials at 157 nm, we have used potential photoresistive materials with aliphatic and aromatic chains in their molecular structure [21–22]. Nylon 6.6 is a good example. The nylon 6.6 monomer has the potential to dissociate into small photofragments in which most of the photoresists used for 193 and 157 nm photolithography are likely to be dissociated.

Mass spectroscopy of nylon 6.6 at 157 nm [24] reveals that even at moderate laser energy there was a complete breaking of the polymeric chain bonds. The following fragments were observed for m/e larger than 30 atomic mass units (amu). The molecular photofragments from the photodissociation of the parent monomer were observed mainly between 20 and 30 amu (Fig. 1). Photofragments with two carbon atoms have a relatively higher probability of being dissociated from the parent monomer than heavier photofragments with four carbon atoms. The polymeric material dissociates into fragments with the predominant mass at 28 amu for both laser wavelengths. Therefore the amide group is mainly involved in the photodissociation process of nylon 6.6 in the VUV at 157 nm, which is the case for wavelengths shorter than 248 nm [21].

Experimental findings suggest that the bound potential energy surfaces of the excited states of the parent molecule correlate with the dissociative potential energy surfaces of the excited states of the molecular photofragments over a wide energy range above 5 eV. Photochemical dissociation of the aliphatic chain is

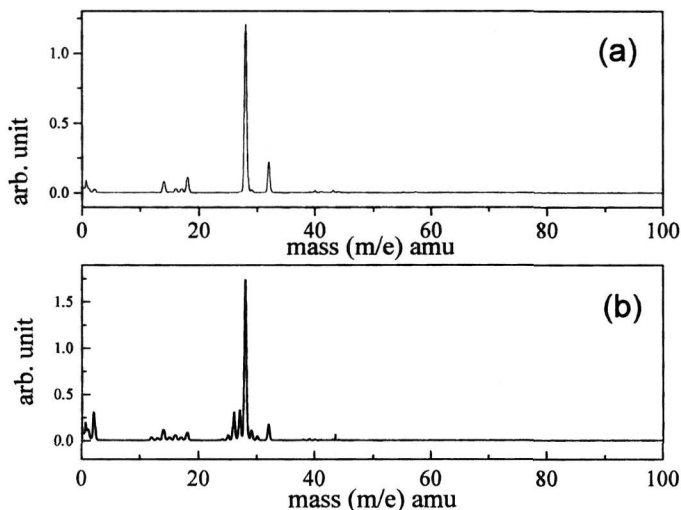


Figure 1 a. Background mass spectrum of nylon 6.6 at 10^{-7} mbar b. Mass spectrum of nylon 6.6 following photofragmentation at 157.6 nm.

the main ablative process at 157 nm. The same response to 157 nm photons has been found in molecules with aromatic structure [22].

The experimental apparatus for obtaining the mass spectrum consists mainly of the molecular fluorine laser source and the vacuum chamber, into which the quadrupole mass spectrometer and sample under investigation were placed (Figs. 2, 3). The sample was a membrane of pure amorphous nylon 6.6, 150 μm thick. The density of the sample was 0.25 gr/cm^3 and it was placed 1 mm apart from the quadrupole mass spectrometer (Baltzers QMG 311) at right angles to its axis (Fig. 2). The all stainless steel 316 vacuum chamber was evacuated to 10^{-6} mbar using a turbomolecular pump.

Laser sources used in these experiments were of the fast-discharge type, which have been described previously [8,9]. The laser head delivers 10 ± 1 mJ per pulse, and the pulse duration was ~ 15 ns at FWHM.

The laser beam was focused on the nylon 6.6 sample, using a quartz lens of 40 cm focal length. After photodissociation of the parent molecule, the molecular photofragments were ionized using an electron gun inside an isopotential chamber (Wetnet). The molecular ions were focused with an Eizen lens, and eventually directed alongside the quadrupole mass filter. The upper detection limit of this filter was 300 amu. After entering the mass filter, ions were deflected at right angles, and detected using a high-gain ($\sim 10^8$) secondary electron multiplier

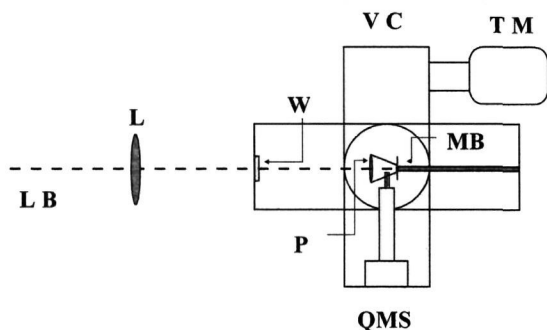


Figure 2 Experimental setup for obtaining mass spectrum of nylon 6.6. LB, laser beam; L, lens; VC, vacuum chamber; TM, turbomolecular pump; W, LiF, window; S, sample; P, photofragments; QMS, quadrupole mass spectrometer.

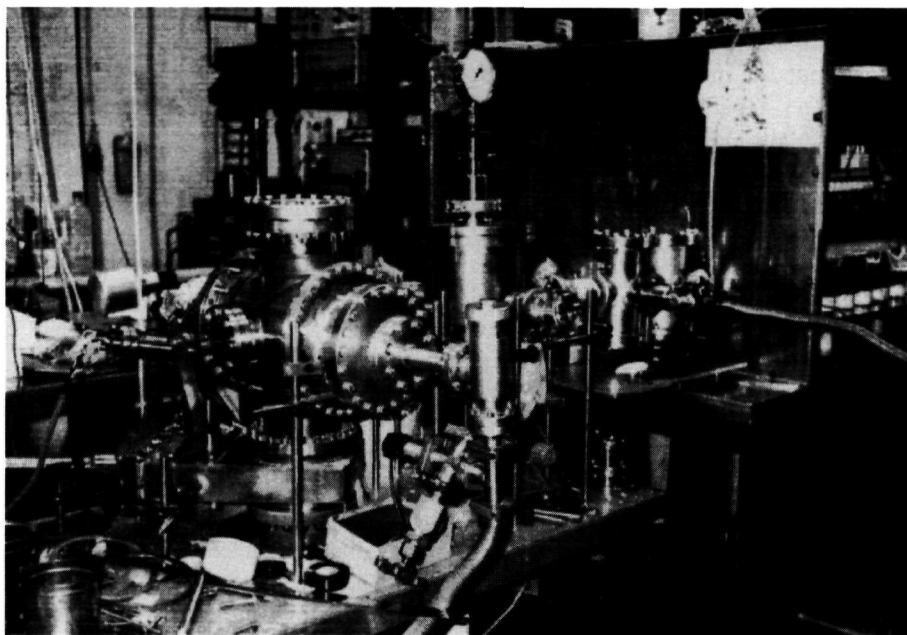


Figure 3 157 nm F₂ laser and mass spectrometer at the NHRF.

(SEM). The signal was then amplified and registered using a boxcar integrator and a computer. Using the same experimental techniques, several polymeric materials have been studied for both VUV absorption below 200 nm and photodissociation dynamic processes under 157 nm illumination. Si-based polymers seem to have the right value of absorbance of $4 \mu\text{m}^{-1}$ at 157 nm and therefore they can be imaged at the usual bilayer thickness of 0.1 μm . However, excessive outgassing at 157 nm at the moment is a serious drawback for their use in 157 nm photolithography [20]. Mass spectroscopic and outgassing studies at 157 nm suggest that a complete bond breaking of the aromatic and linear carbon chains is taking place even at low values of laser energy [20]. However, fluorocarbon polymeric materials seem to have the right absorption coefficient in the VUV and limited outgassing at 157 nm.

III. 157 nm SPECTROSCOPY OF DIATOMIC AND TRIATOMIC MOLECULES

A. OH

Photodissociation of the OH radical was studied at 157 nm via detection of the product H atoms with the resonance fluorescence technique [28]. OH radicals were produced in a fast-flow cell from the reaction between H and NO_2 and subsequently photodissociated by an excimer laser operating on the F_2 emission. The quantum yield for photodissociation of OH was measured and the photodissociation cross section calculated.

B. O_2

Direct photodissociation of molecular oxygen from the $\text{B } ^3\Sigma_u^{-1}$ state have been studied by photoexcitation at 157 nm. The fine structure branching ratios and Doppler profiles of $\text{O}(^3\text{P}_j)$ photofragments were measured using a resonance-enhanced multiphoton ionization technique. Branching ratios of the $\text{O}(^3\text{P}_j)$, $j = 2, 1, 0$, photofragments were measured [29]. The fine structure population of $\text{O}(^3\text{P}_3)$ produced in photodissociation of O_2 at 157 nm was measured in a pump and probe experiment [30]. The population of the ground state ($J = 2$) was found to be 93%, with only 6% in the $J = 1$ level and 1% in $J = 0$. The predominance of $J = 2$ is consistent with direct dissociation on the $\text{B } ^3\Sigma_u$ potential energy surface. Based on available information in the literature, excitation of the $^3\Pi_u$ state and curve crossing to the $^5\Pi_u$ state are ruled out as possible origins of the population with $J < 2$. The populations of $J < 2$ are due to nonadiabatic transitions at large distances. Mechanisms consistent with the data include a Demkov-type interaction, which is caused by coupling by the radial kinetic energy operator. Photodissociation of O_2 at 157 nm has been studied using the photofragmen-

tation translational spectroscopic technique [31]. Two product channels $\text{O}_2 + h\nu \rightarrow \text{O}(^1\text{D}) + \text{O}(^3\text{P})$, $\text{O}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P})$ have been observed. The relative yields and anisotropy parameters of both channels were determined. Anisotropy mixing of dissociation resulting from a perpendicular excitation and a parallel-type excitation has been observed in the dissociation channel $\text{O}_2 + h\nu \rightarrow \text{O}(^3\text{P}) + \text{O}(^3\text{P})$. The observed results can be used to look at the detailed dynamical processes of O_2 dissociation through the Schumann-Runge band.

C. HCl, DCl, CH_3Cl

Hydrogen chloride and methyl chloride were photodissociated at 157 nm [32]. Branching ratios for production of the resulting chlorine atoms in the $^2\text{P}_{1/2}$ state relative to the $^2\text{P}_{3/2}$ state were determined at 157 nm for HCl and CH_3Cl . Doppler profiles of the chlorine fragments have been measured and are interpreted by assuming their anisotropy parameters and translational energies. HCl undergoes a perpendicular optical transition. For CH_3Cl , the transition is a mixture of parallel and perpendicular types at 157 nm.

The H, D, and Cl atoms from the photodissociation of HCl and DCl at 157 were detected by laser-induced fluorescence (LIF) in the vacuum ultraviolet region [33]. Doppler profiles of H and D resonance lines at 121.6 nm in the LIF spectra indicate that the absorption of HCl and DCl at 157 nm is a mixture of perpendicular and parallel transitions. Fine-structure branching ratios were measured for the chlorine atom by LIF. Results suggest that nonadiabatic couplings during the break-up of HCl (DCl) in the excited states play an important role in determining the fine-structure branching ratios.

D. H_2

The photochemical desorption of molecular hydrogen was investigated by F_2 laser irradiation of a $\text{Si}(111)-(1\times 1):\text{H}$ surface [34]. The photon energy of 7.9 eV used was in the region of the broad sigma-sigma* optical transition of SiH centered around 8.5 eV. Molecular dynamics calculations, based on a Tersoff-type interaction potential between silicon and hydrogen, describe the reaction of a hydrogen atom created in a direct bond-breaking process with a neighboring hydrogen atom to form molecular hydrogen. This secondary surface reaction preserves the non-thermal character of the desorption process.

E. OCS

The production of significant concentrations of electrons in high-intensity pulsed-laser photolysis of carbonyl sulfide (OCS) to $\text{S}(^1\text{S})$ at 157 nm has been observed [35]. These results imply a photoionization cross section for $\text{S}(^1\text{S})$ of 2.6×10^{-19}

cm^2 . The authors have measured the quenching of $\text{S}(^1\text{S})$ for a variety of conditions, including incident laser fluences of 100 mJ/cm^2 and initial $\text{S}(^1\text{S})$ densities of $3 \times 10^{16} \text{ cm}^{-3}$. Quenching by electrons can be minimized by adding diluents such as SF_6 or CF_4 . They interpret their observed $\text{S}(^1\text{S})$ decay rates in terms of quenching by $\text{S}(^3\text{P})$ with a rate constant of $3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and by CS [and/or $\text{O}(^3\text{P})$] with a rate constant near $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The measured $\text{S}(^1\text{S})$ lifetime decreases with increasing initial $\text{S}(^1\text{S})$ density, reaching a value of about $1 \mu\text{s}$ at a $\text{S}(^1\text{S})$ density of $3 \times 10^{16} \text{ cm}^{-3}$. The quantum yield for $\text{S}(^1\text{S})$ production was found to be high (near 0.8) and independent of incident laser flux or added diluent pressure. These storage times and production efficiencies are consistent with possible use of the $\text{S}(^1\text{S})$ to $\text{S}(^1\text{D})$ transition as an efficient high-energy-storage laser.

A F_2 laser at 157 nm was also used in a time of flight experiment to measure the translational energy distribution of the fragments of OCS from which the vibrational energy distribution was inferred [36]. It is highly inverted in spite of the fact that the CO bond distances are similar in CO and OCS. Vibrational population inversion, the authors believe, is related to the vibrational structure seen in absorption. A symmetrical type of vibration is excited during the dissociation, which tends to pull both the O and S atoms away from the C atoms. The quasivibrational trajectory ends with the sulfur atom separating, but in the process the CO vibration is strongly excited.

F. H_2O

Polarized photofluorescence excitation spectroscopy of H_2O was described by Andresen et al. [37]. The H_2O^* state (A^1B_1)³ dissociates directly and rapidly with 2.7 eV excess energy. Water molecules were photolyzed by an F_2 laser at 157 nm [38,39]. The nascent OH $^2\Pi_{3/2}$, rotational state distribution, probed via laser-induced fluorescence, reveals a strong preference for populating the upper lambda-doublet component. The population inversion is found to be a function of both the initial temperature of the H_2O and the final rotational state in which the OH radical is formed. These results may provide a simple mechanism for the astronomical OH maser observed by others.

H_2O was excited to the lowest electronic excited state, $^1\text{B}_1$, at 157.6 nm . The OH product state distribution was completely analyzed by special LIF experiments probing the fragment distribution [40]. The OH rotational excitation is relatively low and can be described by a temperature parameter of approximately 500 K independently of the OH vibrational excitation. This is in accordance with former measurements as well as with theoretical calculations. No selective population of the electronic fine-structure levels was observed, which is in agreement with the expectations for a room-temperature experiment. The observed magnitude of the vibrational excitation [$\text{P}(v'' = 0) : \text{P}(v'' = 1) : \text{P}(v'' = 2) : \text{P}(v'' = 3) : \text{P}(v'' = 4) = 59.2 : 33.1 : 6.1 : 1.4 : 0.2$] is smaller than the one calculated. Calcula-

tions predicted the $v'' = 6$ level to be populated, whereas in the experiment, transitions probing the $v'' = 5$ state were not observed.

In similar experiments vibrationally mediated photodissociation, in excitation of an overtone of an O–H stretching vibration, has been used. The vibrationally excited molecule is dissociated with a second photon and initial vibrational excitation alters the decomposition dynamics. For example, the amount of vibrationally excited OH produced in vibrationally mediated photodissociation of H_2O depends strongly on the eigenstate prepared in the vibrational overtone excitation step. This is in agreement with theoretical calculations [41]. The authors describe experiments that exploit this sensitivity to control breaking of the O–H bond in HOD.

Laser-induced fluorescence of microwave-stimulated OH molecules from H_2O photodissociation was investigated as a first step in a series of laboratory experiments to understand features of astronomical OH masers [42]. The inversion between the $\Pi_{3/2} J = 7/2$ lambda-doublet states of OH generated via photodissociation of cold H_2O at 157 nm is shown to be 1.8:1. Within a microwave, Fabry–Perot cavity tuned to the resonance of one of the main hyperfine transitions in this lambda doublet, it is possible to stimulate all inverted OH molecules. The linewidth of the two main microwave transitions is measured as a function of microwave power and interaction time.

G. ICN

Dispersed CN B $^2\Sigma^+ - X^2\Sigma^+$ photofragment fluorescence polarization anisotropies measured [43] following iodo cyanide (ICN) dissociation at 157.6 nm vary widely and apparently erratically with emission wavelength. They cannot be converted directly to CN B $^2\Sigma^+$ rotational alignments because of spectral congestion. A novel linear regression technique is used to extract CN B $^2\Sigma^+$ populations and rotational alignments from fluorescence emission and polarization anisotropy measurements. The authors present a flexible procedure that allows one to consider many models for the population and alignment distributions. Criteria are established to identify the best models. The CN B $^2\Sigma^+$ vibrational branching ratios for $v' = 0:1:2:3:4$ are determined by linear regression to be 0.46:0.25:0.13:0.09:0.07, with a distinct rotational population dependence within each vibrational level. Extracted CN B $^2\Sigma^+$ alignments for $v' = 0, 1, 2$, and 3 are presented, and these range from -0.31 to nearly 0.2 . The alignments vary smoothly with nuclear rotation N' for each v' , demonstrating that the scatter in the measured polarization anisotropies results from vibrational band overlap at different wavelengths. These results show the largest photofragment alignment variation with vibration and rotation that has been measured following a single-photon dissociation process. A model is presented to estimate partial channel CN B($v' = 0$) product populations, and a discontinuity in the experimental $v' = 0$ alignment is considered.

H. HDO

Experimental values for the absorption coefficient and the branching ratio of HDO at 157 nm were compared with theoretical values [44].

I. AsF₃

Visible fluorescence from one-photon excitation of AsF₃ at 157 nm was dispersed and the fluorescing species were attributed to the excited photofragment of AsF₂ [45]. The radiative lifetime of AsF₂^{*} was measured to be $25.5 \pm 1.8 \mu\text{s}$. The quenching rate constant of AsF₂^{*} by AsF₃ was $(1.51 \pm 0.05) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Ultraviolet AsF (A-X) emission is observed from two-photon excitation of AsF₃.

J. O₃

Ozone was generated in pure oxygen ($p \sim 5 \text{ kPa}$), synthetic air ($p \sim 7 \text{ kPa}$), and oxygen–argon mixtures ($p \sim 3 \text{ kPa}$) by irradiation of these gases with the VUV light of a repetitively pulsed (15 Hz) F₂ laser at 157.6 nm with maximum energy of about 4 mJ/pulse [46]. An absorption photometer measurement operating at 253.7 nm (Hg line) determines the ozone concentration as a function of oxygen and/or additive gas pressure, the repetition frequency of the laser, and the wall temperature of the reaction chamber. The temporal development of ozone concentration as a function of these parameters is calculated by means of rate equations for the species O(³P), O₂(X ³Σ_g[−]), O₃ (¹A₁), O(¹D), O₂(a¹Δ_g), O₂(b¹ Σ_g⁺), vibrationally excited O₃^{*} (¹A₁), and the photon distribution. The maximum concentration of O₃ in the sealed-off chamber reaches 1.6% in pure O₂, 4.1% in air, and 1.2% in a 1:5 O₂/–Ar mixture at 3 kPa. The annihilation of O₃ by the wall and temperature-dependent volume processes ($300 \text{ K} < T < 395 \text{ K}$) was studied and experimental and theoretical results were compared.

K. CO₂

The branching ratio was measured for the production of O(³P) in the photodissociation of CO₂ at 157 nm [47]. A gas mixture consisting of CO₂, H₂, and Ar was irradiated with an F₂ excimer laser, while the relative concentration of O(³P) was monitored continuously using atomic resonance fluorescence. The O(¹D) product was removed by either reacting with H₂ or being quenched by CO₂. At high H₂ CO₂ ratio, a residual O(³P) signal persisted due to the nascent photofragments of CO₂. Stern–Volmer analysis indicated that the fraction of O(³P) produced is 5.9%. Control experiments using O₂ and N₂ and O as precursor molecules confirmed this interpretation of the data. A mechanism is proposed based on curve crossing from ²B₂ to ³B₂ potential energy surfaces of CO₂. Since the ¹B₂ state is

bent, a substantial fraction of absorbed energy is initially in bending motion, resulting in a long-lived chaotic trajectory that has many opportunities to cross over to the triplet surface.

$O(2p\ ^3P_j)$ ($j = 2, 1$, and 0) fragments produced in the 157 nm photodissociation of CO_2 were detected by resonance-enhanced multiphoton ionization in a molecular beam [48]. Doppler profiles and fine-structure branching ratios were measured for the oxygen-atom photofragment in the 3P_j states. Doppler profiles were analyzed to give an anisotropy parameter of $\beta = 2.0$ and an internal energy equivalent to 3.9 vibrational quanta of CO. The fine-structure populations were found to be 0.70, 0.16, and 0.14 for $j = 2, 1$, and 0 , respectively. A mechanism is proposed in which complex on the 1B_2 surface undergoes intersystem crossing to the 3B_2 surface. A phase-space model with a constraint on the impact parameter is shown to be consistent with the observed energy release. The nonstatistical fine-structure population could be caused by long-range interactions on the triplet surface. In a bulb experiment, $O(^3P)$ was produced by quenching of $O(^1D)$. The fine-structure populations of the resulting $O(^3P_j)$ were 0.64, 0.25, and 0.11. This state distribution is consistent with a long-lived complex that decays to give statistical products.

Vibrational and rotational distributions of $CO(^1\Sigma_g^+)$ produced in the 157 nm photodissociation of CO_2 have been determined by measuring vacuum-ultra-violet laser-induced fluorescence spectra of the CO photoproduct [49]. The photodissociation of CO_2 is known to occur via two pathways; one yielding $O(^1D)$ and the other yielding $O(^3P)$. Spin conservation and previous experimental studies confirm that dissociation via the $O(^1D)$ channel is the dominant process. The available energy for this channel is sufficient to populate only the ground and first excited vibrational levels of CO. The authors measured the rotational distributions for CO in $v = 0$ and $v = 1$ and found them to be non-Boltzmann. In fact, a highly structured distribution with distinct peaks at $J = 10, 24, 32$, and 39 is observed for CO in $v = 0$. A less structured population is displayed by molecules in $v = 1$. The relative vibrational population ($v = 0/v = 1$) was determined to be 3.7. Doppler spectra of individual rovibronic transitions were also recorded. The profiles have widths in accord with the available translational energy, display the expected v perpendicular to J correlation, and are best described by an isotropic distribution of the velocity vectors with respect to the polarization direction of the dissociation light.

Photodissociation of CO_2 at 157 nm was studied by the photofragment-translational spectroscopy technique. Product time-of-flight spectra were recorded and center-of-mass translational energy distributions were determined [50]. Two electronic channels were observed; one forming $O(^1D)$ and the other $O(^3P)$. With previously determined anisotropy parameters of $\beta = 2$ for the $O(^3P)$ channel and $\beta = 0$ for the $O(^1D)$ channel, an electronic branching ratio of 6% $O(^3P)$ was obtained, consistent with previous results. The translational energy

distribution for the $\text{CO}(\nu) + \text{O}(^3\text{P})$ channel was very broad (over 30 kcal/mol) and appeared to peak near $\text{CO}(\nu = 0)$. The value of $\beta = 2$ for the $\text{O}(^3\text{P})$ channel was confirmed by comparing Doppler profiles, derived from the authors' measured translational energy distribution, with previously measured Doppler profiles. This suggests that the $\text{O}(^3\text{P})$ channel arises from a direct transition to an excited triplet state. The $\text{O}(^1\text{D})$ channel had a structured time-of-flight that related to rovibrational distributions of the CO product. The influence of the excitation of the CO_2 (V_2) bending mode was investigated and shown to have a small but not negligible contribution. Based on a comparison of the authors' data with a previous VUV laser-induced fluorescence study, they obtain as their best estimate of the vibrational branching ratio $\text{CO}(\nu = 0)/\text{CO}(\nu = 1) = 1.9$, for the $\text{CO}(\nu) + \text{O}(^1\text{D})$ channel.

L. SiH

SiH bonds on a hydrogenated Si(111) surface were directly broken by electronic excitation with the 7.9 eV photons of a F_2 laser [51]. Independence of the kinetic energy of the desorbing hydrogen and the linear dependence of the desorption yield on fluence prove the photochemical character of the photoprocess. Solution of the heat diffusion equation indicates a negligible surface heating for the fluences applied.

IV. VUV SPECTROSCOPY OF TRIATOMIC CLUSTERS

Investigation of the properties of small charged or neutral clusters is a subject of growing interest because they bridge the gap between a solid and molecular state of matter [52–59]. Experimental techniques developed to study the clusters and their ions can be classified into two main categories: the optical and the mass spectroscopic. The use of laser spectral techniques such as laser-induced fluorescence or two-photon ionization has been proved unsuccessful for large clusters. This is because both techniques require that the laser-induced transition populate an excited electronic state that survives long enough to be detected by either its fluorescence or its lowered ionization threshold. The large metal clusters have hundred of electronic states within the first few electronvolts. Those states, even if they interact weakly with each other, produce a very dense manifold of vibronic levels. As a result, very complicated spectra arise or radiationless transitions between those levels that quickly lead to a degradation of electronic excitation. On the other hand the detection of cluster ion using mass spectroscopy is free of such problems for both large and small clusters. Mass spectroscopic studies provide basic information about the dissociation energy and kinetics of the

clusters. This can be expressed by the appearance of strong cluster peaks in the mass spectrum denoting the stability of the particularly cluster structures.

It has been observed experimentally that stable clusters can exist in various sizes containing a definite number of atoms for a specific charge. This number is called "magic number" [59–62]. A key problem is to find a sufficiently sensitive detection scheme to detect them. Several models have been proposed to predict or explain the experimentally observed "magic number" [63–68].

Investigation of the electronic structure and dynamics of clusters using vacuum ultraviolet spectroscopy is very important area in the study of clusters. VUV experimental techniques have two advantages: systems with a large band gap can be studied and excitation of inner shell electrons allow us to obtain element-specific information.

The application of a tunable, intense, and coherent VUV light source to molecular spectroscopy and photodissociation chemistry is proposed by K. Yamanouchi [69] to study the high-lying electronically excited states of small jet-cooled molecules and van der Waals clusters. Combination of the VUV laser, generated by two-photon resonance, four-wave sum, or difference frequency mixing scheme, and the free jet expansion techniques is promising to derive precise and substantial information about the level structure and the dynamic processes characteristic of highly excited molecular species excited in the VUV wavelength region.

Moller et al. [70] provide an overview of recent developments in the field of cluster research using VUV radiation. Electronic excitation and relaxation dynamics in helium clusters, and the inner shell photoionization of NaCl clusters produced with a new pick-up cluster source, are also discussed. The near edge absorption structure at the Cl 2p edge contains information on the geometric structure of clusters.

Clusters can be formed in a molecular beam apparatus [71–75], in an oven using the gas aggregation technique [76–80], and by desorption from a surface by ion beam bombardment [81–83], but they can also be the result of photodissociation of a parent molecule [84–87].

Ionization of clusters can be achieved by electron impact [88–90], by one-photon ionization with VUV [91–93] light, by synchrotron radiation or multiphoton ionization with UV or visible laser light [94–96], by liquid metal ion source LMIS [97–99], and by laser-induced field vaporization (LIFV) [68,100–101]. An interesting experimental setup for photoluminescence spectroscopy on van der Waals clusters has been described by R. Karnbach et al. [102]. It consists of a molecular beam apparatus with a cluster beam installed behind a high-intensity VUV synchrotron radiation beamline. Special emphasis was given to the design of a very intense cluster source that can also be used for preparation of quantum clusters (He, H₂). To determine the cluster size, a time-of-flight mass spectrometer can be attached to the setup. In addition, an atomic cross jet is installed in

the experimental chamber that can be used for mass separation or for doping of the clusters. Luminescence light can be recorded with several different detectors or spectrally analyzed with a secondary monochromator equipped with a position-sensitive detector. The pulsed nature of synchrotron radiation provides the basis for time-resolved measurements in the regime 100 ps–3 μ s.

In the work of Wucher et al., neutral atoms and clusters desorbed from a solid germanium surface by 5 keV Ar⁺ ion bombardment [74,103]. Charged clusters were detected directly by time-of-flight mass spectrometry (TOF-MS). The corresponding neutral species were postionized prior to mass and energy analysis. These authors employed two different photoionization schemes. The first was a single-photon ionization process using an F₂ molecular laser as an intense VUV source with photon energy in excess of all relevant ionization potentials. The second was a nonresonant multiphoton ionization process using a high-intensity laser delivering pulses of 250 femtosecond duration at a wavelength of 267 nm. The two processes were compared, and in both cases the available laser pulse energy was sufficient to saturate the ionization of Ge atoms and all detected Ge₂, Ge₃, and up to Ge₇ clusters. This is an indication that the results obtained with both photoionization techniques closely reflect the true cluster sputtering yields and, in particular, are not dominated by photon-induced fragmentation.

Relative yields of sputtered Ge_n clusters are found to obey a power law dependent on the cluster size *n* with an exponent around –6.5 [74]. Kinetic energy distributions exhibit a shift of the maximum toward lower energies with increasing cluster size. Asymptotic decay towards high energies is found to be virtually identical for all measured atoms and clusters. The experiments were repeated on two different single crystalline Ge surfaces <100> and <111> that could be reproducibly amorphized by ion bombardment and reannealed. As a result, the crystalline structure of the ion-bombarded surface was not found to play a significant role in the formation of sputtered clusters.

Neutral clusters of Ag, Al, Nb, and Ta were also formed using the technique of sputtering of polycrystalline surfaces. They were studied experimentally by nonresonant single-photon postionization using a UV or VUV laser beam and time-of-flight mass spectrometry [104]. The mass spectra were recorded at different laser intensities. As a result, photoionization cross sections and the yields of sputtered clusters were determined as a function of the cluster size. The cluster yields roughly exhibit a power law dependence on the cluster size, the exponent of which is found to be inversely correlated with the sputtering yield of the sample. This finding is of particular importance, since it rules out simple statistical combination models to describe the formation of large sputtered clusters. From the yield distributions it is inferred that, depending on the sputtering conditions, up to 46% of the sputtered atoms may be emitted in a bound state. Experimental results were compared with theoretical model descriptions of the cluster formation process.

Neutral silver atoms and small clusters Ag_n ($n = 1 \dots 4$) were generated by bombarding a polycrystalline silver surface with Ar^+ ions of 5 keV [105,106]. The sputtered particles were ionized by a crossed electron beam or by the F_2 single photon at 7.9 eV from a pulsed VUV laser that permits nonresonant single-photon ionization (SPI) of all investigated species and is subsequently detected by a quadrupole mass spectrometer. Photoionization cross sections were evaluated from the laser intensity dependence of the measured mass spectrum. SPI ionization cross sections do not vary dramatically between silver atoms and different clusters. As a consequence, fragmentation influences encountered in previous studies with longer-wavelength lasers are practically eliminated from the determination of yields and kinetic energy distributions of the sputtered clusters. The resulting relative cluster sputtering yields (normalized to the yield of silver atoms) exhibit a power law dependence on the cluster size n according to $n^{-\delta}$ with exponents of δ ranging from 4.3 to 7.4 depending on the nature and the bombarding energy of the primary ions. Kinetic energy distributions of the sputtered neutral atoms and clusters are evaluated up to clusters containing seven atoms. Asymptotic decay of the energy distribution towards high-emission energies becomes steeper from Ag to Ag_3 and remains practically constant for larger clusters. By in situ combination of both ionization mechanisms, absolute values of the ratio $\sigma(e)(\text{Ag}_n)/\sigma(e)(\text{Ag})$ between the electron impact ionization cross sections of silver clusters and atoms could be determined for a fixed electron energy of 46 eV. These values can then be used to calibrate previously measured relative ionization functions. By calibrating the results using literature data measured for silver atoms, we present absolute cross sections for electron impact ionization of neutral Ag_2 , Ag_3 , and Ag_4 as a function of the electron energy between threshold and 125 eV.

V. LASER-INDUCED FLUORESCENCE AND MASS SPECTROSCOPY OF MERCURY DIATOMIC AND TRIATOMIC CLUSTERS ASSISTED BY LASER LIGHT AT 157.6 nm

Laser-induced fluorescence of the mercury clusters Hg_2 and Hg_3 in the spectral range from 300 to 510 nm has been obtained from the dissociation of HgBr_2 at 157.6 nm with an F_2 molecular laser. The excitation process involves two-photon absorption, which dissociates the molecule at 15.76 eV total photon energy with the subsequent formation of metallic clusters [85].

Photodissociation of HgBr_2 at 157.5 nm using the F_2 molecular laser was proven to be an efficient method for producing small mercury clusters Hg_2 and

Hg_3 in their excited states [107]. Although photodissociation of mercury halides by the ArF excimer laser at 193 nm (and at other excimer and dye lasers wavelengths) has been extensively studied [108–113], there are no reports of metallic cluster formation at this wavelength. In addition, a detailed study of the spectroscopy of the triatomic mercury clusters in electric discharges has been investigated well before VUV optical excitation [114,115].

The electronic structure of HgBr_2 and the HgBr molecules indicates that three-dipole allowed transitions can be excited between the low-lying electronic states of the HgBr_2 molecule, $1\ ^1\Pi_u$, $1\ ^1\Sigma_u^+$, $2\ ^1\Sigma_u^+$, and its ground state $1\ ^1\Sigma_g^+$ [116–119]. VUV excitation at 157.5 nm stimulates the $1\ ^1\Sigma_g^+ \rightarrow 2\ ^1\Sigma_u^+$ transition, (Fig. 4).



The $2\ ^1\Sigma_u^+$ state of HgBr_2 at 7.88 eV correlates with the the $D(^2\Pi_{3/2})$ and $C(^2\Pi_{1/2})$ states of HgBr and the 2P state of Br.

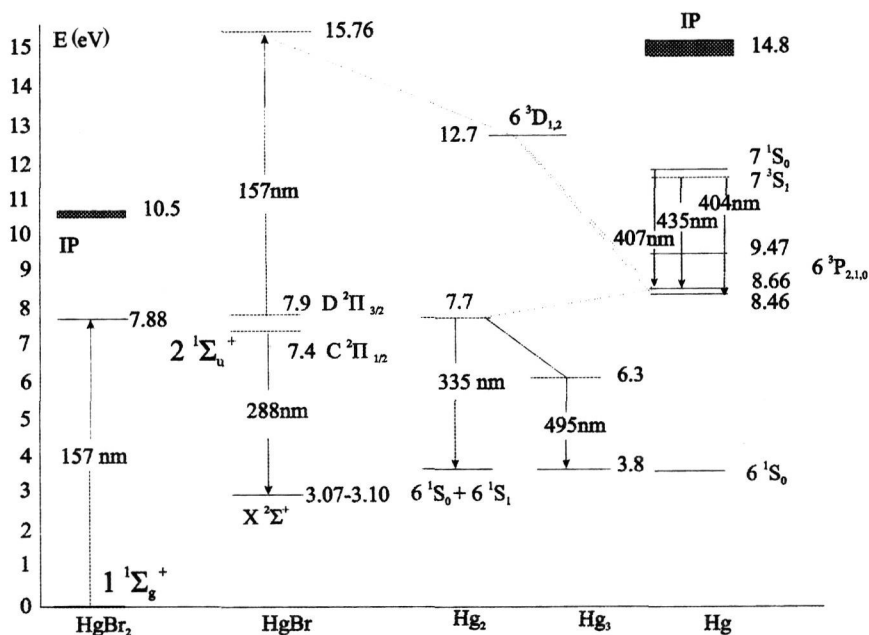
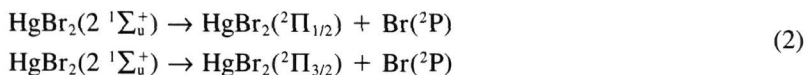
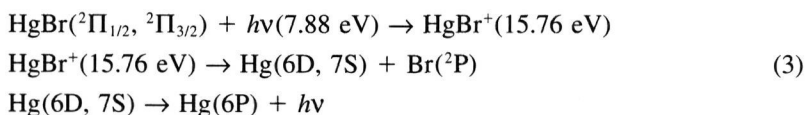


Figure 4 Energy pathway of formation of mercury atoms from the dissociation of HgBr_2 at 157.6 nm.

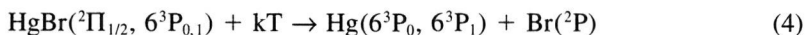


The $2\ ^1\Sigma_u^+$ electronic state is strongly correlated with $D(^2\Pi_{3/2})$ and $C(^2\Pi_{1/2})$ electronic excited states of the HgBr diatomic following dissociation to HgBr and Br.

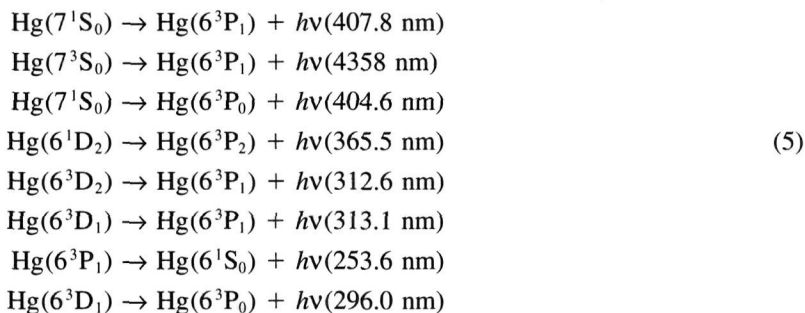
The small energy gap between the D state and the available energy from one photon at 157.5 nm can be bridged thermally at high temperatures. Therefore a fraction of the population is transferred to the D state [120] and the remaining part to the C state of HgBr. From the C and D states the molecules can either radiate to the X state or can absorb a second 157.5 nm photon and photoionize the HgBr molecule. The $C \rightarrow X$ transition at 285 nm is the strongest transition in the spectrum, while the $D \rightarrow X$ transition at 265 nm is ~ 10 times weaker. The overall absorption cross section at 157.5 nm has been found to be $(4.5 \pm 2.6) \times 10^{-16} \text{ cm}^2$ [107] in the temperature range between 40 and 90°C. This is considerably higher than the value of the absorption cross section at 193 nm, which has been found to be $3.8 \times 10^{-17} \text{ cm}^2$ [121]. However, the theoretical calculations of Wadt [116] predict that the absorption cross section between $1\ ^1\Sigma_g^+$ and $2\ ^1\Sigma_u^+$ states at 157 nm should be smaller than the absorption cross section between $1\ ^1\Sigma_g^+$ and $1\ ^1\Sigma_u^+$ states at 193 nm by a factor of 35. The above discrepancy between the experimental and theoretical values indicates that other loss mechanisms than the absorption between the $1\ ^1\Sigma_g^+$ and $2\ ^1\Sigma_u^+$ states should play a major part in the annihilation of VUV photons by the HgBr₂ molecules. These absorption mechanisms include one-step ionization of HgBr from the C and D states and two-step ionization of HgBr₂ from its ground state. The C and D states of HgBr at 7.88 eV correlate with the $6^3P_{0,1}$ metastable states of Hg either via one-photon absorption and subsequent deexcitation to the $6^3P_{0,1}$ states:



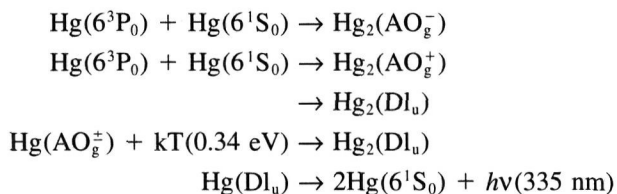
or through thermal dissociation according to



The energy gap between the $^2\Pi_{3/2}$ state of HgBr and the $\text{Hg}(6^3P_0)$ state of mercury is between 0.58 and 0.53 eV [122,123]. Therefore, at 300°C less than $\sim 0.1\%$ of the population of the diatomic is thermally dissociating to the $\text{Hg}(6^3P_0) + \text{Br}(^2P)$ atoms. The observed emissions at 404.6, 435.8, 407.8, 312, 313, 296, 365, 366, and 254 nm are from the allowed dipole transitions from the 7S, 6D, and 6P states of mercury

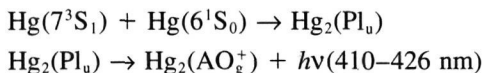


The kinetic processes associated with the formation of $\text{Hg}_2(\text{AO}_g^\pm)$ from $6^3\text{P}_{0,1}$ and 6^1S_0 states have been studied in detail [124]. Spectroscopy of the Hg_2 molecule has been given by the work of Niefer et al. [125], Callear et al. [126], and Drullinger et al. [127]. A collision between a metastable mercury atom 6^3P_0 and a ground state atom 6^1S_0 can create the mercury dimer Hg_2 in its excited states $\text{AO}_g^\pm$. Collision between a 6^3P_0 mercury atom and a 6^1S_0 ground state atom can form a mercury dimer either in the AO_g^+ state or in the Dl_u state, depending on the thermal energy available. The $\text{AO}_g^\pm$ states 2800 cm^{-1} below the optically active Dl_u state either can act as an energy reservoir for the formation of the Hg_3 cluster or can thermally populate the Dl_u state of Hg_2 , which gives the 335 nm band through de-excitation to the dissociative ground state.



The spectral lines detected in the region between 410 and 426 nm originate from the de-excitation of the $\text{Hg}_2(\text{Pl}_u)$ Rydberg state to the AO_g^+ state.

The $\text{Hg}_2(\text{Pl}_u)$ state is created through a collision between an $\text{Hg}(7^3\text{S}_1)$ atom with a ground state atom $\text{Hg}(6^1\text{S}_0)$

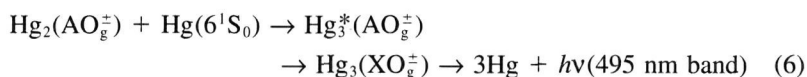


This de-excitation channel is another pathway of populating the reservoir of the $\text{AO}_g^\pm$ states.

The 335 nm band is much narrower than the one previously reported from electric discharges [128]. Transition from the $6^3\text{D}_{1,2}$ manifold to the 6^3P_1 state is located at 313 nm. Transitions from the same $6^3\text{D}_{1,2,3}$ manifold to the 6^3P_2 state were recorded as well. Two new progressions of lines at 349 nm, 353 nm,

and 357 nm, and at 371 nm, 375 nm, and 380 nm had been observed. The first manifold has been observed previously in HgBr discharges and was attributed to the presence of N₂. However, the spectra have been recorded alongside of and sideways to the laser beam and the presence of N₂ should be excluded from our laser system.

The intensity of these spectral lines varies with temperature (they are very intense above 250°C). Their temporal behavior suggests that they are transitions from excited states of the Hg₂ cluster formed by the highly excited states to Hg without attempting any assignments. The dependence of the intensity of mercury lines at 404.6 nm and 366 nm on temperature, together with rate of formation arguments, suggest that these lines might originate from emissions from the highly excited states of Hg₂: for example, (Hg(7¹D₂) + Hg(6¹S₀)) to lower ones. As far as the progression of lines around 380 nm is concerned, there is a dependence between the intensity of these lines and the intensity of mercury lines at 365 nm that originate from the 6³D manifold. The remaining part of the spectrum between 385 and 400 nm consists of a series of lines. Temporal evolution of these spectral lines suggests that they originate from transitions from the excited states of the mercury triatomic Hg₃. Similar long-lived states have been observed previously around 446 nm and have been attributed to the complex potential surfaces of Hg₃. The lifetime of excited states of the Hg₂ cluster is believed to be short [129], and the long decay rates observed are attributed instead to clusters' rates of formation in their excited states. This argument is also supported by the temporal evolution of the 335 nm band. Therefore, considering that the rates of formation are small, the long lifetimes could be attributed to Hg₃ clusters because of the complicated structure of their potential surfaces. Strong perturbations present in the Hg₃ molecule, alongside tunneling effects, could be the source of long decay rates. The broad continuum in the blue-green region of the spectrum taken in a mercury vapour column with maximum at 495 nm has been assigned to emission from the Hg₃ molecules [127]. The same band has been observed previously by Cefalas et al. [107] by laser-induced fluorescence. Niefer et al. [125], using selective excitation in mercury vapor, had assigned the observed absorption between 415 and 510 nm to the presence of the mercury cluster Hg₃. The sideways fluorescence of the 495 nm band between 480 nm and 510 nm indicates some vibrational structure with a maximum at 494 nm. The formation of Hg₃ originates from the collision of an Hg₂ molecule in its first excited state with an Hg atom in its ground state, since the band is observed even without the use of a buffer gas.



The emitted radiation at 495 nm is highly directional and concentrated. Its superfluorescence nature [107] was manifested by the appearance of blue-green spots

on a screen even 50 cm away from the fluorescence cell. Similar kinds of blue-green spots have been observed by Shingenari et al. [130] at 404 and 407 nm during the photodissociation of HgBr_2 at 193 nm. The appearance of these spots suggests that at 495 nm the gain exceeds the absorption for this excitation scheme. The blue-green spots do not appear on a regular basis, indicating that thermal gradients inside the heat pipe oven might cause strong refractive index variations. For excitation schemes that involve electrical discharges or selective excitation of mercury atomic levels at high temperatures, extension of the band towards the red is due to the formation of mercury clusters $\text{Hg}_n (n > 3)$.

VI. BISTATE QUANTUM SWITCHING IN MERCURY TRIATOMIC CLUSTERS

Quantum beats with a period from 25 to 100 ns have been observed in mercury triatomic clusters following de-excitation from excited electronic states of volcanic shape to the ground electronic state (Fig. 5). Observation of the quantum beats can be explained if we assume that the dynamic surface of the Hg_3 cluster has a symmetry of a double well. This is true for a large number of X_3 systems, including Cu_3 [131], Na_3 [132], P_3 , As_3 , Sb_3 , Bi_3 [133] Ca_3 , and Sc_3 [134]. Formation of the Hg_3 clusters was also observed by optical spectroscopy by J. Koperski et al. [135].

Because the vibrational and the electronic parts of the total wavefunctions are not any longer separable for the Hg_3 molecular system, the excited electronic states have a complex volcanic structure. The presence of potential energy barriers is the source of tunneling effects of the optical electron. In the simplest case, potential energy barriers exhibit saddle points with double minima. A double barrier can exhibit resonances where total transmission of electrons is taking place even for energies below the height of the potential barrier. This accounts for zero dispersion of the particle wave packet. It is responsible for the observed long duration of the quantum beats because the molecule oscillates, trapped between a symmetrical and an antisymmetrical wavefunction without any reflection losses. The presence of the double minima causes splitting of vibrational eigenfunctions in a symmetrical and an antisymmetrical component. The reason is the introduction of an additional translational symmetry in the total Hamiltonian of the system [136]. The amount of the energy split between the two parts depends on the molecular parameters and energy separation of the optical electron from the top of the potential barrier (Fig. 6). Energy splitting is related to the beat period. Hence the period of the quantum beat depends on the electron energy relative to the top of the barrier. It increases with increased energy separation from the top of the double barrier because total transmission probability of the optical electron through the energy potential barrier depends on its energy separation from the top of the potential barrier as well. The potential barrier over which

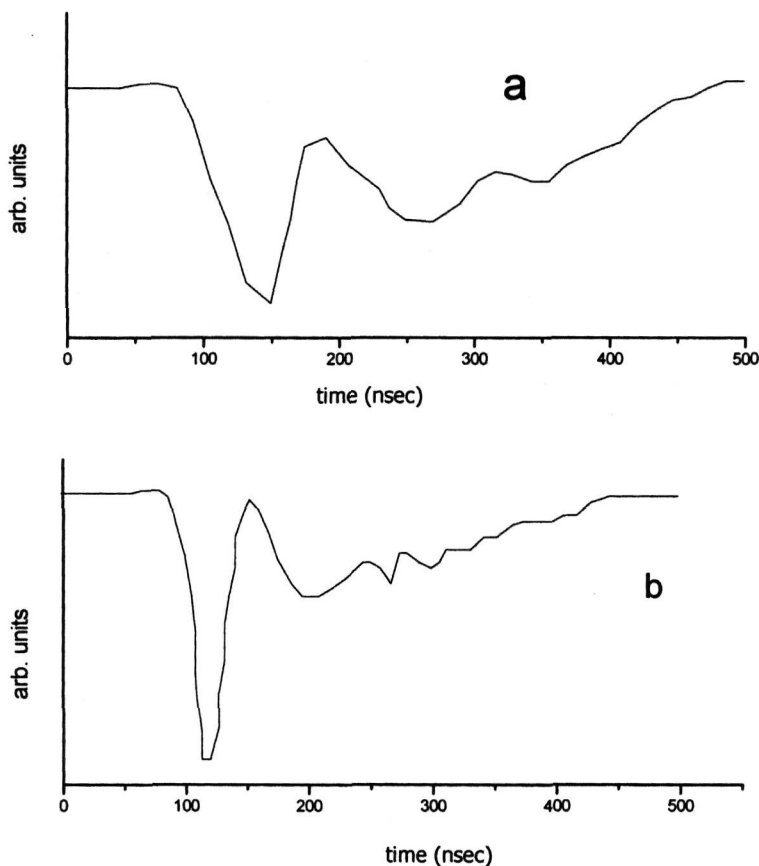


Figure 5 a. Mode competition at 445 nm. b. Mode competition at 446.9 nm.

quantum beats were observed was found to be 0.05 eV deep [137]. As a result, selective excitation in Hg_3 clusters could modulate the period of the quantum beat and the electron transmission probability through the potential barrier of the excited electronic states. This process simulates the switching function of a quantum transistor with its gate driven by light.

Double-charged Hg_3 clusters following the photodissociation of the HgBr_2 were observed using the mass spectroscopic technique. The parent HgBr_2 was expanded from a molecular beam apparatus, after being heated in the molecular beam chamber. Parent molecules were crossed with the F_2 molecular laser focused in the molecular beam with a MgF_2 lens with focal length of 20 mm (Fig. 7). The Hg_3 clusters were formed according to the mechanism described previ-

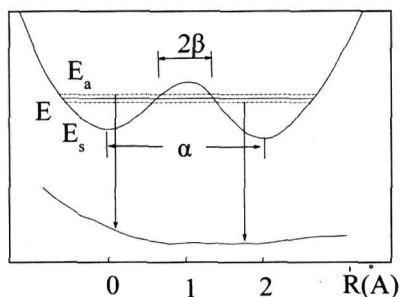


Figure 6 Potential energy surface for the 445 nm band. Symmetry splitting is indicated. Optical transitions are taking place between the excited and ground electronic states of the mercury trimer.

ously, in their excited electronic states and were observed with the quadrupole mass spectrometer (Fig. 8). Double-charged triatomic mercury clusters were the smallest ever observed (Fig. 7). Berchignac et al. [77], using a different experimental technique, observed double-charged mercury clusters containing up to five atoms of mercury. The theoretical calculations performed by Tomanek [67] give for the number n in Hg_n^{2+} the value of 300; Jentsch et al. found $n = 8$ [68], and Sattler et al. found $n = 9$ [80].

To interpret the observed quantum beats and make the proper assignments,

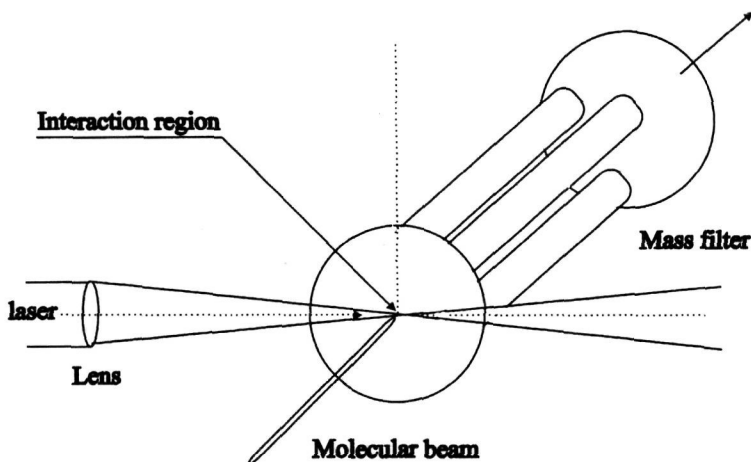


Figure 7 Geometry of detection of trimer mercury clusters. Direction of the laser light is perpendicular to the direction of the molecular beam and quadrupole mass filter.

a simple formula was derived that relates the experimentally measured splitting of the vibrational levels of the excited triatomic molecule to the shape of the potential surfaces showing double minima. The presence of the double minima imposes translational symmetry in the potential energy surfaces. We will consider the simplest case: the potential energy surface is symmetrical with respect to an axis that passes from the point equidistant from the two minima (Fig. 6). For the sake of simplicity, we will consider only one dimension x . The symmetry of the potential surface implies the relation

$$U(x + a) = U(x) \quad (7)$$

where a is the distance between the two minima of the potential surface $U(x)$.

Therefore we can introduce the translation operator $\hat{T}(a)$, which translates the space coordinate of a point at x by a distance a , and for a wave function $\Psi(x)$ we have

$$\hat{T}(a)\psi(x) = \psi(x + a) \quad (8)$$

Expanding $\psi(x + a)$ in a Taylor series around the point x we have

$$\psi(x + a) = \sum_0^{\infty} \frac{1}{m!} \frac{d^m \psi(x)}{dx^m} a^m = \left(\sum_0^{\infty} \frac{1}{m!} a^m \nabla^m \right) \psi(x) = \hat{T}(a)\psi(x) \quad (9)$$

and the translation operator $\hat{T}(a)$ is of the form

$$\hat{T}(a) = \exp(a\nabla) \quad (10)$$

The action of the translational operator on the potential function is of the form

$$\hat{T}(a)U(x) = U(x + a) = U(x) \quad (11)$$

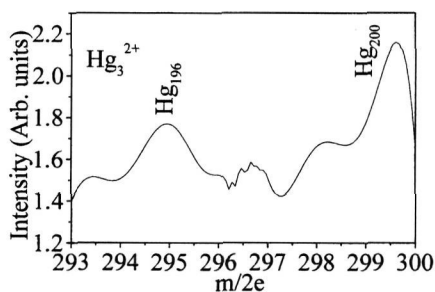


Figure 8 Mass spectrum of mercury doubly ionized trimer clusters.

Using the relationship above it is easy to see that the translation operator commutes with the potential energy of the system and the kinetic part of the Hamiltonian $\hat{H}$, where

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \quad (12)$$

Therefore the translational operator commutes with the Hamiltonian of the system and the operators $\hat{H}$ and $\hat{T}(a)$ have the same set of wave functions, $\psi(x)$.

Suppose now that the eigenfunction $\psi(x)$ of the translation operator $\hat{T}(a)$ corresponds to the eigenvalue $T(a)$

$$\hat{T}(a)\psi(x) = T(a)\psi(x) \quad (13)$$

We can prove easily that

$$\hat{T}^m(a) = T(ma) \quad (14)$$

and if we write $T(a)$ in the form

$$T(a) = \exp(i\phi(a)) \quad (15)$$

it can be proved that

$$\phi(a) = ka \quad (16)$$

$$\begin{aligned} \hat{T}(a)\psi(x) &= \exp(ika)\psi(x) = \psi(x + a) \\ \psi(x + a) &= \exp(ika)\psi(x) \end{aligned} \quad (17)$$

Therefore the eigenfunctions $\psi(x)$ of the Hamiltonian and the translation operator obey the so-called translation property of Eq. (17) (Bloch equations). The zero-order approximation now of the wave function $\psi(x)$, $\psi_0(x)$ enables the calculation of the energy eigenvalues of Eq. (12) to the first order.

$$\hat{H} = \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + U(x) \right] \psi_0(x) = E_1 \psi_0(x) \quad (18)$$

where the subscripts 0 and 1 refer to the zero and first-order approximations for the wave function and the energy. From Eq. (18) we find

$$E_1 = \frac{\int \psi_0^*(x) [-(\hbar^2/2m)(d^2/dx^2) + U(x)] \psi_0(x) dx}{\int \psi_0^*(x) \psi_0(x) dx} \quad (19)$$

The potential function can be expanded now around x in a Taylor series

$$U(x) = \sum_a U_a(x) \exp(ika) \quad (20)$$

Therefore Eq. (19) becomes

$$E_1 = I \int \psi_0^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_a U_a(x) \exp(ika) \right] \psi_0(x) dx \quad (21)$$

where

$$I = \left\{ \int \psi_0^*(x) \psi_0(x) dx \right\}^{-1}$$

Now we have

$$E_1 = I \left\{ \int \psi_0^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_{a' \neq a} U_{a'}(x) \exp(ika') + U_a(x) \exp(ika) \right] \psi_0(x) dx \right\} \quad (22)$$

taking into account the translational properties of the potential function $U(x)$ and the wave function $\psi(x)$ Eq. (17), we have

$$\begin{aligned} E_1 &= I \left\{ \int \psi_0^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_{a' \neq a} U_{a'}(x - a') \right] \psi_0(x) dx \right. \\ &\quad \left. + U_a(x - a) \int \psi_0^*(x) \psi_0(x) dx \right\} \\ E_1 &= I \left\{ \int \psi_0^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_{a' \neq a} U_{a'}(x - a') \right] \psi_0(x - a') \exp(ika) dx \right. \\ &\quad \left. + U_a(x - a) \int \psi_0^*(x) \psi_0(x) dx \right\} \quad (23) \\ &= E_a + F(a, k) \exp(ika) \end{aligned}$$

where we have denoted

$$E_a = U_a(x - a)$$

and

$$F(a, k) = I \left\{ \int \psi_0^*(x) \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \sum_{a' \neq a} U_{a'}(x - a' - a) \right] \psi_0(x - a) dx \right\} \quad (24)$$

The last integral describes the exchange of energy between the two parts of the barrier: right of the symmetry axis where the wave function is $\psi_0(x)$ and left of the symmetry axis where the wave function is $\psi_0(x - a)$.

The energy E_1 therefore depends quasicontinuously on the wave vector k and its real part changes from $E_{1 \min}$ to $E_{1 \max}$ as k changes:

$$\begin{aligned}
 E_1 &= E_a + F(a, k)\cos(ka) \\
 E_{1\min} &= E_a + F(a, k) \\
 E_{1\max} &= E_a + F(a, k)
 \end{aligned}
 \tag{25}$$

Hence the amount of the energy splitting as the particle moves through the double barrier is $\Delta E = 2F(ak)$. The mass of the cluster m is related to the energy E_1 through the equation

$$m^{-1} = \left| \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \right| \tag{26}$$

and therefore

$$m^{-1} = \left| \frac{1}{\hbar^2} \frac{dF}{dk^2} \cos(ka) - 2 \frac{dF}{\hbar^2 dk} a \sin(ka) - \frac{Fa^2}{\hbar^2} \cos(ka) \right| \tag{27}$$

For a heavy particle like the triatomic mercury trimer, we do not expect the exchange integral to change a great deal with the wave vector k . Therefore, Eq. (27) becomes

$$m = \left| \frac{2\hbar^2}{\Delta E a^2 \cos(ka)} \right| \tag{28}$$

Equation 28 is our final result and relates the energy-splitting ΔE of the vibrational levels to the mass (m) of the triatomic and the distance (a) between the two minima of the potential surface. The observed period of the quantum beats (Fig. 9) is related to the energy-splitting ΔE of the vibrational levels by

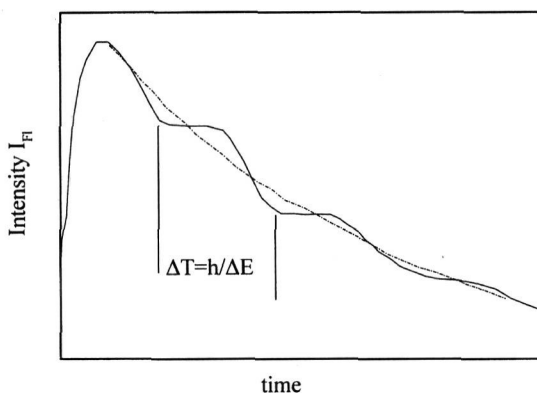


Figure 9 Time evolution of transitions between excited and ground electronic states of mercury trimer.

Table 1 Period T of Quantum Beats for the Three Emission Bands of Mercury Triatomic Cluster

Band λ (nm)	Emission λ (nm)	Q B Period T (ns)
385	385, 387, 389	75, 50, 25
445	445, 447, 449, 451, 453	100, 75, 50, 25
485	482, 485, 488	300, 100, 75, 50, 25

The second column shows the wavelength of emission from different vibronic levels.

the uncertainty relation $\Delta E \Delta T = h$. For a typical beat distance of 75 ns, $\Delta E = 5 \times 10^{-6}$ eV. From Eq. 28 we find that this value corresponds to a distance a between the minima of the potential surface of 0.2 nm for $k = 53 \times 10^{10} \text{ m}^{-1}$.

A formula that relates the molecular parameters to the amount of splitting ΔE is given by

$$\Delta E = \frac{\Delta E_0}{\pi} \exp \left(- \int_{-\beta}^{\beta} |k| dx \right) \quad (29)$$

where β is the distance between two turning points (Fig. 6), ΔE_0 the energy difference between two neighboring vibronic levels near the top of the barrier, and k is the wave vector related to the reduced cluster mass and it is given by $k = (2m/\hbar^2 (E - U))^{1/2}$. $(E - U)$ is the distance of a vibronic level from the top of the barrier. Eq. (29) can be used to test the validity of our approximations, which have been derived from Eq. (28).

From spectroscopic data the energy difference between two neighboring vibrational levels is 0.04 eV. Hence, the first vibronic level below the top of the potential barrier will be situated below the top of the barrier at the most by the same amount of energy of 0.04 eV. Therefore, the wave vector k associated with the vibronic level near the top of the potential barrier is $\sim 3.6 \times 10^{11} \text{ m}^{-1}$. For a splitting ΔE of 5×10^{-6} eV, the distance 2β is estimated to be 0.02 nm and the distance α between the two minima is 0.2 nm. The period of the observed quantum beats for the three emission bands is indicated in Table 1. Fourier transform analysis of the signals indicates multiple frequencies over the same vibrational level. This is due to the fact that the potential energy surfaces are not symmetrical in space. Quantum beats are observed only for the vibrational levels indicated in Table 1 because symmetry splitting and tunneling is taking place only for those levels close to the top of the potential barrier, in agreement with the theoretical model. The transmission coefficient T of a particle for a double

barrier described by the $U_0 \cosh^{-2}(x/2\beta)$ dependence in a region near its top is given by the equation

$$T = \frac{\sinh^2(2\pi k\beta)}{\sinh^2(2\pi k\beta) + \cosh^2[\frac{1}{2}\pi\sqrt{32mU_0}\eta^{-2}\beta^2 - 1]} \quad (30)$$

From Eq. (30) if $1 - 32mU_0\eta^{-2}\beta^2 = (2n + 1)^2$, then the transmission coefficient is equal to 1. In this case the particle is transmitted through the barrier with zero reflection losses. For $n = 1$, $U_0 = 10^{-3}$ eV, in agreement with our experimental results regarding the high of the potential barrier over which beat oscillations were observed. The process simulates the switching properties of a molecular transistor with its gate driven by light.

REFERENCES

1. JR Woodworth, JK Rice. An efficient, high-power F_2 laser near 157 nm. *J Chem Phys* 69:2500–2504, 1978.
2. JK Rice, AK Hays, JR Woodworth VUV emissions from mixtures of F_2 and the noble gases-A molecular F_2 laser at 1575 Å. *Appl Physics Letts* 31:31–33, 1977.
3. H Pummer, K Hohla, AM Diegelmann, JP Reilly. Discharge pumped F_2 laser at 1580 Å. *Optics Communics* 28:104–106, 1979.
4. AC Cefalas, C Skordoulis, M Kompitsas, CA Nicolaides. Gain measurements at 157 nm in an F_2 pulsed discharge molecular laser. *Optics Communics* 55:423–426, 1985.
5. VN Ishchenko, SA Kochubei, AM Razhev. High-power efficient vacuum ultraviolet F_2 laser excited by an electric discharge. *Sov J Quantum Electron.* 16:707–709; translated from *Kvantov Elektron Moskva* 13:1072–1075, 1986.
6. M Ohwa, M Obara. Theoretical evaluation of high-efficiency operation of discharge-pumped vacuum-ultraviolet F_2 lasers. *Appl Physics Letts.* 51:958–960, 1987.
7. K Yamada, K Miyazaki, T Hasama, T Sato. High-power discharge-pumped F_2 molecular laser. *Appl Physics Letts* 54:597–599, 1989.
8. C Skordoulis, S Spyrou, AC Cefalas. Gain and saturation measurements in a discharge excited F_2 laser using an oscillator amplifier configuration. *Appl Physics B* 51:141–145, 1990.
9. C Skordoulis, E Sarantopoulou, S Spyrou, AC Cefalas. Amplification characteristics of a discharge excited F_2 laser. *J Modern Optics* 37:501–509, 1990.
10. AA Kuznetsov, SS Sulakshin. An F_2 laser-excited by a high-power proton-beam. *Kvantov Elektron* 18:22–22, 1991.
11. M Kakehata, T. Uematsu, F. Kannari, M. Obara. Efficiency characterization of vacuum ultraviolet molecular fluorine (F_2) laser (157 nm) excited by an intense electric-discharge. *IEEE J Quantum Electron* 27:2456–2464, 1991.

12. M Kakehata, CH Yang, Y Ueno, F Kannari. Gain and saturation intensity measurements of a discharge pumped F₂ laser at high-excitation rates. *Appl Physics Letts* 61:3089–3091, 1992.
13. FTJL Lankhorst, HMJ Bastiaens, PJM Peters, WJ Witteman. High specific laser output energy at 157-nm from an electron-beam-pumped He/Ne/F₂ gas-mixture. *Appl Physics Letts* 63:2869–2871, 1993.
14. FTJL Lankhorst, HMJ Bastiaens, PJM Peters, WJ Witteman. Long pulse electron beam pumped molecular F₂ laser. *J Appl Physics* 77:399–401, 1995.
15. HMJ Bastiaens, SJM Peeters, X Renard, PJM Peters, WJ Witteman. Long pulse operation of an x-ray preionized molecular fluorine laser excited by a pre pulse-main pulse system with a magnetic switch. *Appl Physics Letts* 72:2791–2793, 1998.
16. N Rizvi, D Milne, P Rumsby, M Gower. Laser micromachining—new developments and applications. *Proc SPIE* 3933:261–270, 2000.
17. JC White, HG Craighead, RE Howard, LD Jackel, OR Wood. VUV laser photolithography. *AIP Conf Proc* 119:324–329, 1984.
18. S Nagai, T Enami, T Nishisaka, J Fujimoto, O Wakabayashi, H Mizoguchi. Development of kHz F₂ laser for 157 nm lithography. In: *Digest of Papers, Microprocesses and Nanotechnology '99. International Microprocesses and Nanotechnology Conference*. Tokyo, Japan: Japan Society of Applied Physics, 234:64–65 1999.
19. T Hofmann, JM Hueber, P Das, S Scholler. Revisiting F₂ laser for DUV micro-lithography. *Proc SPIE* 3679:541–546, 1999.
20. AC Cefalas, E Sarantopoulou, E Gogolides, P Argitis. Absorbance and outgassing of photoresist polymeric materials for UV lithography below 193 nm including 157 nm lithography. *Microelectron Engin* 53:123–126, 2000.
21. AC Cefalas, N Vassilopoulos, Z Kollia, E Sarantopoulou, C Skordoulis. Mass spectroscopic studies and ablation characteristics of nylon 6.6 at 248 nm. *Appl Phys A* 70:21–28, 2000.
22. AC Cefalas, E Sarantopoulou, P Argitis, E Gogolides. Mass spectroscopic and degassing characteristics of polymeric materials for 157 nm photolithography. *Appl Physics A* 69: 929–933, 1999.
23. AC Cefalas, P Argitis, Z Kollia, E Sarantopoulou, TW Ford, AD Stead, A Maranka, CN Danson, J Knott, D Neely. Laser plasma x-ray contact microscopy of living specimens using a chemically amplified epoxy resist. *Appl Phys Letts* 72:25–27, 1998.
24. AC Cefalas, E Sarantopoulou. 157 nm photodissociation of polyamides, *Microelect. Engin* 53:464–468, 2000.
25. TM Bloomstein, MW Horn, M Rothschild, RR Kunz, ST Palmacci, RB Goodman. Lithography with 157 nm lasers. *J Vac Sci Technol B* 15:2112–2116 1997.
26. RR Kunz, TM Bloomstein, DE Hardy, RB Goodman, DK Downs, JE Curtin. Outlook for 157 nm resist design. *SPIE* 3678:13–23, 1999.
27. I. Petsalakis, G Theodorakopoulos, Electronic states of CF⁺. *Chem Phys* 254:181–186, 2000.
28. RJ Cody, C Moralejo, JE Allen Jr. Photodissociation of the hydroxyl radical (OH) at 157 nm. *J Chem Phys* 95: 2491–2496, 1991.
29. Y Matsumi, M Kawasaki. Fine-structure branching ratios of the O(3Pj) atomic frag-

- ments from photodissociation of oxygen molecules at 157 and 193 nm. *J Chem Phys* 93:2481–2486, 1990.
30. YL Huang, RJ Gordon. The multiplet state distribution of O(3Pj) produced in the photodissociation of O₂ at 157 nm. *J Chem Phys* 94:2640–2647, 1991.
 31. JJ Lin, DW Hwang, YT Lee, XM Yang. Photodissociation of O₂ at 157 nm—experimental-observation of anisotropy mixing in the O₂ + hν → O(P – 3) + O(P – 3) channel. *J Chem Phys* 109:1758–1762, 1998.
 32. Y Matsumi, PK Das, M Kawasaki. Doppler spectroscopy of chlorine atoms generated from photodissociation of hydrogen-chloride and methyl-chloride at 157-nm and 193-nm. *J Chem Phys* 92:1696–1701, 1990.
 33. K Tonokura, Y Matsumi, M Kawasaki, S Tasaki, R Bersohn. Photodissociation of hydrogen-chloride at 157 and 193 nm—angular-distributions of hydrogen-atoms and fine-structure branching ratios of chlorine atoms in the 2Pj levels. *J Chem Phys* 97:8210–8215, 1992.
 34. U Wetterauer, A Pusel, P Hess. VUV photodesorption of molecular-hydrogen from the hydrogenated silicon(III) surface. *Chem Phys Lett* 300:397–402, 1999.
 35. JK Rice, JR Woodworth. High-intensity laser photolysis, of OCS at 157 nm: S^{1/S} production photoionization, and loss. *J Appl Phys* 50:4415–4421, 1979.
 36. GS Ondrey, S Kanfer, R Bersohn. The collinear photodissociation of OCS at 157 nm. *J Chem Phys* 79:179–184, 1983.
 37. P Andresen, GS Ondrey, EW Rothe, B Titze. The photodissociation of H₂O at 157 nm: full internal state distributions and alignment of nascent OH(X²Π) radicals. In: J Eichler, W Fritsch, IV Hertel, N Stolterfoht, U Wille, eds. 13th International Conference on the Physics of Electronic and Atomic Collisions. Berlin, West Germany: 1983.
 38. P Andresen, GS Ondrey, B Titze. Creation of population inversions in the Lambda doublets of OH by the photodissociation of H₂O at 157 nm: a possible mechanism for the astronomical maser. *Phys Rev Lett* 50:486–488, 1983.
 39. P Andresen, EW Rothe. Polarized LIF spectroscopy of OH formed by the photodissociation of H₂O by polarized 157 nm light. *J Chem Phys* 78:989–990, 1983.
 40. K Mikulecky, K Heinz-Gericke, FJ Comes. Decay dynamics of H₂O(¹B₁): full characterization of OH product state distribution. *Chem Phys Lett* 182:290–296, 1991.
 41. RL Vander-Wal, JL Scott, FF Crim. Selectively breaking the O-H bond in HOD. *J Chem Phys* 92:803–805, 1990.
 42. H Wurps, H Spiecker, JJ ter-Meulen, P Andresen. Laser induced fluorescence measurements of microwave stimulated OH molecules from H₂O photodissociation. *J Chem Phys* 105:2654–2659, 1996.
 43. JA Guest, F Webster. Strong fragment alignment variation with internal state from ICN dissociation at 157.6 nm: linear regression modelling of CN B² sigma⁺ products *J Chem Physics* 86:5479–5490, 1987.
 44. N Shafer, S Satyapal, R Bersohn. Isotope effect in the photodissociation of HDO at 157.5 nm. *J Chem Phys* 90:6807–6808, 1989.
 45. C Ye, M Suto, LC Lee, TJ Chuang. Radiative lifetime and quenching rate constant of AsF₂⁺ fluorescence. *J Phys B* 22:2527–2529, 1989.
 46. B Freisinger, U Kogelschatz, JH Schafer, J Uhlenbush, W Viol. Ozone production in oxygen by means of F₂ laser at X = 157.6 nm. *Appl Phys B* 49:121–129, 1989.

47. Zhu Yi-Fei, RJ Gordon. The production of $O(^3P)$ in the 157 nm photodissociation of CO_2 . *J Chem Physics* 92:2897–2901, 1990.
48. Y Matsumi, N Shafer, K Tonokura, M Kawasaki, H Yu Lin, RJ Gordon. Doppler profiles and fine structure branching ratios of $O(^3P_j)$ from photodissociation of carbon oxide at 157 nm. *J Chem Phys* 95:7311–7316, 1991.
49. RL Miller, SH Kable, PL Houston, I Burak. Product distributions in the 157 nm photodissociation of CO_2 . *J Chem Phys* 96:332–338, 1992.
50. A Stolow, YT Lee. Photodissociation dynamics of CO_2 at 157.6 nm by photofragment translational spectroscopy. *J Chem Phys* 98:2066–2076, 1993.
51. A Pusel, U Wetterauer, P Hess. Direct breaking of SiH-surface bonds with 157 nm laser radiation. *Laser Optom* 31:48–50, 1999.
52. JM Soler, MR Beltran, K Michaelian, IL Garzon, P Ordejon, D Sanchez-Portal, E Artacho. Metallic bonding and cluster structure. *Phys Rev B* 61:5771–5780, 2000.
53. K Michaelian, N Rendon, IL Garzon. Structure and energetics of Ni, Ag, and Au nanoclusters. *Phys Rev B* 60:2000–2010, 1999.
54. U Meier, SD Peyerimhoff, F Grein. Ab initio MRD-CI study of neutral and charged Ga_2 , Ga_3 , and Ga_4 clusters and comparison with corresponding boron and aluminum clusters. *Z Phys D* 17:209–224, 1990.
55. *Surface Science* 156:1986; *Z Phys D* 3:1986.
56. A Dixon, C Colliex, R. Ohana, P Sudraud, J Van-de-Walle. Field-ion emission from liquid tin. *Phys Rev Letts* 46:865–868, 1981.
57. K Gamo, Y Inomoto, Y Ochiai, S Namba. B, Sb and Si liquid metal alloy ion sources for submicron fabrication. *Jpn J Appl Phys* 21:415–420, 1982.
58. C Brechignac, M Broyer, P Cahuzac, G Delacretaz, P Labastie, L Woste. Stability and ionization threshold of doubly charged mercury clusters. *Chem Phys Lett* 118:174–178, 1985.
59. AR Waugh. Current-dependent energy spectra of cluster ions from a liquid gold ion source. *J Phys D* 13: L203–208, 1980.
60. S Mukherjee, KH Bennmann. On the stability of charged metallic clusters. *Surface Sci* 156:580–583, 1985.
61. G Durand, JP Daudey, JP Malrieu. Singly and doubly charged clusters of (S^2) metals. Ab initio and model calculations on Mg_n^+ and Mg_n^{++} ($n \leq 5$). *J Phys* 47:1335–1346, 1986.
62. S Martrenchard, C Jouviet, C Lardeux-Dedonder, D Solgadi. Observation of very small doubly charged homogeneous para difluorobenzene clusters. *J Chem Phys* 94:3274–3275, 1991.
63. K Sattler. The physics of microclusters. *Adv Solid State Phys* 23:1–12, 1983.
64. O Eht, K Sattler, E Recknagel. Magic numbers for sphere packings: experimental verification in free xenon clusters. *Phys Rev Lett* 47:1121–1124, 1981.
65. JG Gay, BJ Berne. Computer simulation of Coulomb explosions in doubly charged Xe microclusters. *Phys Rev Lett* 49:194–198, 1982.
66. P Pfau, K Sattler, R Pflaum, E Recknagel. Observation of doubly charged lead clusters below the critical size limit for Coulomb explosion of sphere configurations. *Phys Lett A* 104A:262–263, 1984.

67. D Tomanek, S Mukherjee, KH Bennemann. Simple theory for the electronic and atomic structure of small clusters. *Phys Rev B* 28:665–673, 1983.
68. Th Jentsch, W Drachsel, JH Block. Stability of doubly charged homonuclear trimeric metal clusters. *Chem Phys Lett* 93:144–147, 1982.
69. K Yamanouchi. Tuneable vacuum ultraviolet laser ideal light for spectroscopy of atoms, molecules, and clusters. *Electron Spectrosc Rel Phenom* 80:267–270, 1996.
70. T Moller, ARB Decastro, K Vonhaefen, A Kolmakov, T Laarmann, Lofken, C Nowak, F Picucci, M Riedler, C Rienecker, A Wark, M Wolff. Electronic-structure and excited-state dynamics of clusters—what can we learn from experiments with synchrotron radiation. *Electron Spectrosc Rel Phenom* 103:185–191, 1999.
71. OF Hagen. Formation of silver clusters in nozzle expansions. *Z Phys D* 20:425–8, 1991.
72. C Brechignac, M Broyer, P Cahuzac, G Delacretaz, P Labastie, L Woste. Size dependence of linear-shell autoionization lines in mercury clusters. *Chem Physics Letts* 120:559–563, 1985.
73. C Brechignac, M Broyer, P Cahuzac, G Dalacretaz, P Labastie, L Woste. Stability and ionization threshold of double charged mercury clusters. *Chem Phys Lett* 118:174–278, 1985.
74. R Heinrich, A Wucher. Yields and energy distributions of sputtered semiconductor clusters. *Nuclear Instrum Methods Physics Res* 140:27–38, 1998.
75. MA Ratner. Kinetics of cluster growth in expanding rare-gas jet. *Low Temp Physics* 25:266–273, 1999.
76. W Schulze, B Winter, J Urban, I Goldenfeld. Stability of multiply charged silver clusters. *Z Phys D* 4:379–381, 1987.
77. W Schulze, B Winter, I Goldenfeld. Generation of germanium clusters using the gas aggregation technique: stability of small charged clusters. *J Chem Physics* 87:2402–2403, 1987.
78. W Schulze, B Winter, I Goldenfeld. Stability of multiply positively charged homonuclear clusters. *Phys Rev B* 38:12937–12941, 1988.
79. A Hoareau, P Melinon, B Cabaud, D Rayane, B Tribollet, M Broyer. Fragmentation of singly and doubly charged lead clusters. *Chem Phys Lett* 143:602–608, 1988.
80. K Sattler, J Muhlbach, O Echt, P Pfau, E Rechnagel. Evidence for Coulomb explosion of doubly charged microclusters. *Phys Rev Lett* 47:160–163, 1981.
81. VI Matveev, PK Khabibullaev. Sizes and charges of clusters produced in the process of ion sputtering of a metal. *Doklady Physics* 44:789–792, 1999.
82. A Wucher, Z Ma, WF Calaway, MJ Pellin. Yields of sputtered metal clusters: the influence of surface structure. *Surface Sci* 304:L439–444, 1994.
83. A Wucher, M Wahl, H Oechsner. The mass distribution of sputtered metal clusters. *Exp Nuclear Instrum Methods Physics Res* 83:73–78, 1993.
84. S Nishigaki, W Drachsel, JH Block. Photon-induced field ionization mass spectrometry of ethylene on silver. *Surface Sci* 37:389–409, 1979.
85. C Skordoulis, E Sarantopoulou, SM Spyrou, C Kosmidis, AC Cefalas. Laser induced fluorescence (LIF) of Hg_2 and Hg_3 via dissociation of HgBr_2 at 157 nm. *Z Phys D* 18:175–180, 1991.

86. L Wiedeman, H Helvajian. Laser photodecomposition of sintered $\text{Yb}_2\text{Cu}_3/\text{O}_{6+x}$: ejected species population distributions and initial kinetic energies for the laser ablation wavelengths 351, 248, and 193 nm. *J Appl Phys* 70:4513–4523, 1991.
87. Proceedings Laser Induced Chemistry Conference, 18–22 Sept. 1989, Bechyne, Czechoslovakia. *Spectrochim Acta* 46A(4):1990.
88. M Ovchinnikov, BL Grigorenko, KC Janda, VA Apkarian. Charge localization and fragmentation dynamics of ionized helium clusters. *J Chem Phys* 108:9351–9361, 1998.
89. C Brechgnac, M Broyer, P Cahuzac, G Dalacretaz, P Labastie, L Woste. Stability and ionization threshold of double charged mercury clusters. *Chem Phys Lett* 118: 174–278, 1985.
90. D Rayane, P Melinon, B Cabaus, A Hoareau, B Tribollet, M Broyer. Electronic properties and fragmentation processes for singly and doubly charged indium clusters. *J Chem Phys* 90:3295–3299, 1989.
91. E Ruhl, PG F Bisling, B Brutschy, H Baumgartel. Photoionization of aromatic van der Waals complexes in a supersonic jet. *Chem Phys Lett* 126:232–237, 1986.
92. JR Grover, EA Walters, ET Hui. Dissociation energies of the benzene dimer and dimer cation. *J Phys Chem* 91:3233–3237 1987.
93. W Kamke, B Kamke HU Kiefl, IV Hertel. Photoionization and fragmentation of $(\text{N}_2\text{O})_N$ clusters. *J Chem Phys* 84:1325–1334, 1986.
94. B Bescos, B Lang, J Weiner, V Weiss, E Wiedenmann, G Gerber. Real-time observation of ultrafast ionization and fragmentation of mercury clusters. *Eur Phys J D* 9:399–403, 1999.
95. T Baumert, R Thalweiser, V Weiss, G Gerber. Time-resolved studies of neutral and ionized Na_n clusters with femtosecond light pulses. *Z Phys D* 26:131–134, 1993.
96. JA Booze, T Baer. On the determination of cluster properties by ionization techniques. *J Chem Physics* 96:5541–5543, 1992.
97. A Dixon, C Colliex, R Ohana, P Sudraud, J Van de Walle. Field-ion emission from liquid tin. *Phys Rev Lett* 46:865–868, 1981.
98. J Van de Walle, P Joyes. Study of Bi_n^{p+} ions formed in liquid-metal ion sources. *Phys Rev B* 35:5509–5513, 1987.
99. Y Gotoh, T Kashiwagi, H Tsuji, J Ishikawa. Empirical relation between electric field at the ionization point and emission current of liquid copper, gold, germanium, and tin ion sources. *Appl Phys A* 64:527–532, 1997.
100. W Drachsel, T Jentsch, KA Gingerich, JH Block. Observation of doubly charged triatomic cluster ions in field evaporation. *Surface Sci* 156:173–182, 1985.
101. K Hata, M Ariff, K Tohji, Y Saito. Selective formation of C_{20} cluster ions by field evaporation from carbon nanotubes. *Chem Phys Lett* 308:343–346, 1999.
102. R Karnbach, M Joppien, J Stapelfeldt, J Wormer, T Moller. CLULU—an experimental setup for luminescence measurements on van der Waals clusters with synchrotron radiation. *Rev Sci Instrum* 64:2838–2849, 1993.
103. A Wucher, R Heinrich, RM Braun, KF Willey, N Winograd. Vacuum ultraviolet single-photon versus femtosecond multiphoton ionization of sputtered germanium clusters. *Rapid Commun Mass Spectrom* 12:1241–1245, 1998.

104. A Wucher, M Wahl. The formation of clusters during ion-induced sputtering of metals. *Nucl Instrum Methods Phys Res B* 115:581–589, 1996.
105. D Koch, M Wahl, A Wucher. Electron-impact and single-photon ionization cross-sections of neutral silver clusters. *Z Phys D* 32:137–144, 1994.
106. M Wahl, A Wucher. VUV Photoionization of sputtered neutral silver clusters. *Nucl Instrum Methods Physics Res B* 94:36–46, 1994.
107. AC Cefalas, C Skordoulis, C Nicolaides. Superfluorescent laser action around 495nm in the blue–green band of the mercury trimer Hg_3 . *Optics Commun* 60:49–54, 1986.
108. TA Cool, JA McGarvey Jr, AC Eriandson. Two-photon excitation of mercury atoms by photodissociation of mercury halides *Chem Phys Lett* 58:108–113, 1978.
109. W Luthy, R Schiimiele, T Gerber. Spectral properties of a HgBr_2 photodissociation laser. *Phys Lett* 88:450–452, 1982.
110. Nai-Ho Cheung, JA McGarvey Jr, AC Eriandson, TA Cool. The vibrational distribution of HgBr ($X^2 \Sigma$) molecules formed by photodissociation of HgBr_2 at 193 nm *J Chem Phys* 77:5467–5474, 1982.
111. T Efthimiopoulos, D Zevgolis, J Katsenos, D Zigos. Laser action from (B2E-X2E) HgBr induced by UV laser multiphoton dissociation of HgBr_2 measurements and experimental results. *Proc SPIE* 3423:68–71, 1998.
112. EJ Schimitschek, JE Celto, JA Trias. Mercuric bromide photodissociation laser *Appl Phys Lett* 31:608–610, 1977.
113. JH Schloss, JG Eden. Excited-state absorption in HgBr *Appl Phys Lett* 55:1282–1284, 1989; see also C Whitehurst, TA King. Multiphoton excitation of mercury atoms by photodissociation of HgX_2 ($X = \text{Cl}, \text{Br}, \text{I}$). *J Phys B* 20:4053–4051, 1987.
114. RE Drullinger, MM Hessel, EW Smith. Experimental study of mercury molecules. *J Chem Phys* 66:5656–66, 1977.
115. AB Callear, KL Lai. Electronic absorption spectra of metastable dimers and trimers in optically excited mercury vapour. The carrier of the green emission. *Chem Phys Lett* 64:100–104, 1979.
116. WR Wadt. The electronic structure of HgCl_2 and HgBr_2 and its relationship to photodissociation *J Chem Phys* 72:2469–2478, 1980.
117. C Duzy, HA Hyman. Radiative lifetimes for the B to X transition in HgCl , HgBr , and HgI . *Chem Phys Lett* 52:345–348, 1977.
118. J Tellinghuisen, JG Ashmore. The B to X transition in $^{200}\text{Hg } ^{79}\text{Br}$. *Appl Phys Lett* 40:867–869, 1982.
119. J Husain, JR Wiesenfeld, RN Zare. Photofragment fluorescence polarization following photolysis of HgBr_2 at 193 nmJ. *Chem Phys* 72:2479–2483, 1980.
120. AK Rai, SB Rai, OK Rai. Ultraviolet bands in diatomic mercury bromide. *J Phys B* 16:1907–1913, 1983.
121. BE Wilcomb, R Burnham, N Djew. UV absorption cross section and fluorescence efficiency of HgBr_2 . *Chem Phys Lett* 75:239–242, 1980.
122. SH Linn, WB Tzeng, JM Jr Brom, CY Ng. Molecular beam photoionization study of HgBr_2 and HgI_2 . *J Chem Phys* 78:50–61, 1983.
123. J Maya. Fluorescence yields of metal halide vapors excited by photodissociation. *Appl Phys Lett* 32:484–486, 1978.

124. M Stock, EW Smith, RE Drullinger, MM Hessel. Relaxation of the mercury 6^2P_0 and 6^3P states J Chem Phys 67:2463–2469, 1977.
125. RJ Niefer, J Supronowicz, JB Atkinson, L Krause. Laser-induced fluorescence of $Hg_2 H1_u$ excimer molecules. Phys Rev A 34:1137–1142, 1986; J Supronowicz, RJ Niefer, JB Atkinson, L Krause. Laser-induced fluorescence spectrum arising from $G0_u^+ X0_g^+$ bound-free transitions in Hg_2 L. J Phys B19:1153–1164, 1986; RJ Niefer, J Supronowicz, JB Atkinson, L Krause. Laser-induced fluorescence from the H, I, and J states of Hg_2 . Phys Rev A 35:4629–4238, 1987; RJ Niefer, J Supronowicz, JB Atkinson, L Krause. Laser-induced fluorescence spectroscopy of the Hg_3 excimer. Phys Rev A 34:2483–2485, 1986; RJ Niefer, JB Aktinson, L Krause. Vibrational structure of some Hg_2 fluorescent bands. J Phys B16:3767–3773, 1983.
126. AB Callear, KL Lai. Electronic absorption spectra of metastable dimers and trimers in optically excited mercury vapour: the carrier of the green emission. Chem Phys Lett 64, 100, 1979; AB Callear, KL Lai. Vibrational structure of Rydberg transitions of metastable mecury dimers. Chem Phys Lett 75:234, 1980; AB Callear, KL Lai. Transient immediates in the flash photolysis of mercury vapour. Dimers, trimers and the enigmatic 2480 AA bands. Chem Phys 69:1, 1982; AB Callear, DR Kendall. A violet emission from optically excited mercury vapour: kinetics of the formation and decay of excited dimers and trimers. Chem Phys Lett 64:401, 1979; AB Callear, DR Kendall. Combination of metastable and ground-state mercury atoms into ungerade dimer states. Chem Phys Lett 70:215, 1980; AB Callear, DR Kendall. Luminescence from mixtures of mercury vapour and nitrogen following pulsed excitation with resonance radiation. Chem Phys 57:65, 1981.
127. RE Drullinger, MM Hessel, EW Smith. A theoretical analysis of mercury molecules. J Chem Phys 66:5656–5666, 1977; EW Smith, RE Drullinger, MM Hessel, J Cooper. A theoretical analysis of mercury molecules. J Chem Phys 66:5667–5681, 1977.
128. ER Mosburg, MD Wilke. Excimer densities and destruction mechanisms in a high pressure pure mercury positive column. J Chem Phys 66:5682–5693, 1977.
129. PJ Hay, TH Dunning, RC Raffeneti. Electronic states of Zn_2 ab initio calculations of a prototype for Hg_2 . J Chem Phys 65:2679–2689, 1976.
130. T Shigenari, F Uesugi, H Takuma. Superfluorescent laser action at 404.7 nm from the transition of a mercury atom produced by photodissociation of $HgBr_2$ by an ArF laser. Opt Lett 7:362–364, 1982.
131. SR Langhoff, CW Bauschlicher Jr, SP Walch, BC Laskowski. Ab initio study of the ground state surface of Cu_3 . J Chem Phys 85:7211–7215, 1986.
132. M Broyer, G Delacretaz, P Labastie, JP Wolf, L Woste. Spectroscopy of vibrational ground-state levels of Na_3 . J Phys Chem 91:2626–2630, 1987.
133. K Balasubramanian, K Sumathi, D Dai. Group V trimers and their positive ions: the electronic structure and potential energy surfaces. J Chem Phys 95:3494–34505, 1991.
134. SP Walch, CW Bauschlicher Jr. On 3d bonding in the transition metal trimers: the electronic structure of equilateral triangle Ca_3 , Sc_3 , Sc_3^+ , and Ti_3^+ . J Chem Phys 83: 5735–5742, 1985.
135. J Koperski, JB Atkinson, L Krause. First observations of laser-excited Hg_3 and Hg_2 Rg spectra in a supersonic expansion beam. J Mol spectrosc 187:181–192, 1998.

136. LD Landau, EM Lifshitz. Quantum mechanics. Oxford, England: Pergamon Press, 1981.
137. AC Cefalas, SM Spyrou, E Sarantopoulou. Observation of vibronic–electronic interaction in mercury triatomic clusters via real time quantum beats. *Laser Ultrafast Proc* 4:175–181, 1991.

