

CONF-910402--15

DE91 012058

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submitted for publication in the ACS Symposium Series
Isotope Effects in Chemical Reactions and Photodissociation Processes

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NEGATIVE ION FORMATION BY RYDBERG ELECTRON TRANSFER: ISOTOPE-DEPENDENT RATE CONSTANTS

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The formation of negative ions during collisions of rubidium atoms in selected ns and nd Rydberg states with carbon disulfide molecules has been studied for a range of effective principal quantum numbers ($10 \leq n^* \leq 25$). For a narrow range of n^* near $n^* = 17$, rate constants for CS_2^- formation are found to depend upon the isotopic composition of the molecule, producing a negative ion isotope ratio (mass 78 to mass 76, amu) up to 10.5 times larger than the natural abundance ratio of CS_2 isotopes in the reagent. The isotope ratio is found to depend strongly upon the initial quantum state of the Rydberg atom and perhaps upon the collision energy and CS_2 temperature.

In recent years there has been rapid growth in the study of the properties and collision dynamics of atoms in highly excited (Rydberg) states (1). Collisions involving these "Rydberg atoms" are important in many processes which occur in high-energy environments such as the interstellar medium, plasmas, and combustion flames. In addition to their importance in such processes, Rydberg atoms have also been recently used as tools in the laboratory to probe low-energy electron-molecule interactions and, in particular, low energy electron attachment to molecules (2). In a recent publication (3) we reported an unusually large isotope dependence of rate constants for CS_2^- ion formation during collisions between Cs (ns , nd) Rydberg atoms and CS_2 molecules. For a narrow range of effective principal quantum number near $n^* = 17$ we found that rate constants for formation of $^{32}\text{S}^{12}\text{C}^{34}\text{S}^-$ ions were up to 4.5 times greater than those for $^{32}\text{S}^{12}\text{C}^{32}\text{S}^-$ formation. Preliminary measurements using jet-cooled CS_2 molecules suggested that the ratio of rate constants for the two isotopes was also dependent upon the CS_2 temperature (3). The origin of the isotope dependence, however, remains unexplained. In this paper we present the results of a recent

study of the isotope dependence of rate constants for CS_2^- formation during collisions of Rb ($ns\ nd$) Rydberg atoms with CS_2 molecules.

Rydberg Electron Transfer (RET). Several unique properties of Rydberg atoms (summarized in Table I) make them quite useful as tools for probing low-energy electron-molecule interactions. When one electron in an atom is excited to an orbital of large principal quantum number, n , its average distance from the nucleus and inner electrons (together referred to as the "core") is much larger than the range of interaction between a charged particle and a neutral molecule.

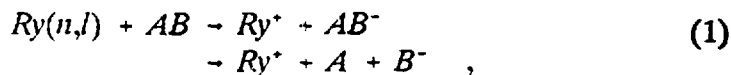
Table I. Properties of Hydrogen-like Rydberg Atoms

Property	n-dependence	$n=1$	$n=25$	$n=50$
Bohr radius r_n (Å)	$n^2 a_0$	0.53	331	1325
rms velocity of electron v_{rms} (cm s ⁻¹)	v_0/n	2.2×10^8	8.8×10^6	4.4×10^6
binding energy E_n (eV)	R/n^2	13.6	2.2×10^{-2}	5.4×10^{-3}

Therefore, during a collision between a highly excited Rydberg atom and a neutral molecule, the excited electron and the core behave as independent particles. The interaction between the Rydberg electron and a molecule is then essentially that of a free electron interacting with a molecule. This idea forms the basis for the "free electron model" which has been used to theoretically model Rydberg atom-molecule collisions (4,5).

One advantage of using Rydberg atoms to probe electron-molecule interactions is that the root-mean-square velocity, v_{rms} , of the Rydberg electron decreases as n increases (see Table I). Thus at large n , it is possible to produce electrons with subthermal velocities, which is not feasible with alternative methods. Since the binding energy of the electron to the core also decreases rapidly as n increases ($\propto 1/n^2$), it is easily removed from the atom during collisions and may attach to a colliding molecule, providing a method for studying very low-energy electron attachment processes.

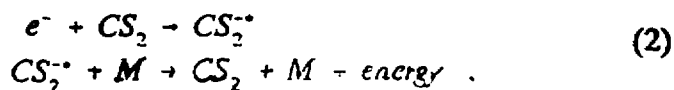
In general, for Rydberg electron transfer (RET) reactions of the type



it has been shown (2) that, for large values of n ($n \geq 25$), rate constants for

negative ion production agree well with rate constants for free electron attachment and are in accord with the "free electron model." However, for lower values of n , the Rydberg electron and ion core no longer behave as independent particles and the "free electron model" is no longer applicable. In these cases, interactions between the nascent negative and positive (Rydberg core) ions formed by RET become important and may greatly affect the rates for ion production (6-10). In particular, for thermal collision energies, the strong Coulombic attraction between the nascent positive and negative ions (which becomes more important at lower n) may prevent the ions from separating, resulting in a rapid decrease in the rate constants for ion production as n decreases (6-10). More interesting perhaps are several recent studies which have shown that such interactions may also lead to stabilization of negative ions which otherwise have very short autodetachment or dissociation lifetimes, including CS₂ (3,10,11), O₂ (10,12), CH₃NO₂ (13), HI (13), and DI (13). The CS₂ molecule is especially interesting in this regard.

Carbon Disulfide. The electron affinity of CS₂ is known to be positive and the CS₂⁻ ion has been observed by many workers using a variety of techniques (14-20). Using photodetachment electron spectroscopy, Oakes and Ellison (21) recently determined the electron affinity of CS₂ to be 0.895 ± 0.020 eV. The neutral CS₂ molecule has the electronic configuration . . . (5σ_g)²(4σ_u)²(6σ_g)²(5σ_u)²(2π_u)⁴(2π_g)⁴ and is linear in its ¹Σ_g⁺ ground state (D_{∞h} symmetry). The lowest unoccupied orbital of CS₂ is a doubly degenerate π_u orbital in the linear molecule. However, due to vibronic coupling (the Renner-Teller effect), the degeneracy of the π_u orbital is lifted as the molecule bends and it evolves into two nondegenerate orbitals (a₁ and b₁) for the bent configuration (C_{2v} symmetry) (22). The a₁ orbital is lowered in energy relative to the π_u orbital (23) and therefore the ground state of CS₂⁻ is expected to be bent with a bond angle of ~132° (24). A negative ion produced by capture of an electron into the π_u orbital will therefore be very short-lived (on the order of a bending vibrational period) unless energy is somehow removed from the ion to stabilize it in a bent configuration. Measurements of electron attachment rate constants for CS₂ in the presence of various buffer gases (25) are consistent with this notion. The measured attachment rates are well-described in terms of a two-step three-body (Bloch-Bradbury) attachment mechanism (25),



where a third body (buffer gas, M) collisionally stabilizes the short-lived temporary negative ion.

Several groups have previously studied Rydberg electron transfer to carbon disulfide (3,10,11). During collisions of K (nd) Rydberg atoms ($10 < n < 20$) with CS₂, Kalamarides *et al.* (11) observed production of both long-lived CS₂⁻ ions and free electrons. These authors suggested that free

electron production resulted from Rydberg electron capture into short-lived CS_2^- states which underwent rapid autodetachment, as discussed above. The observation of long-lived CS_2^- ions suggested that, for the intermediate values of n studied, a fraction of the nascent CS_2^- ions may be stabilized by energy transfer with the Rydberg core before autodetachment occurs. Since the average Bohr radius of the Rydberg electron is proportional to n^2 (see Table I) the nascent ions are formed in closer proximity at lower n and stabilization is expected to become more efficient. In this case the Rydberg core acts as a "built-in" third body during the collision. In accord with this hypothesis, the Rice group (11) found that rate constants for production of stable CS_2^- ions increased as n was decreased from 18 to 12. However, a significant fraction of the long-lived CS_2^- ions were found to undergo field-induced detachment in moderate ($1\text{-}3\text{ kV cm}^{-1}$) electric fields (11). These results suggested that perhaps more than one mechanism for production of long-lived ions was important and that ions in different electronic or vibrational states may be produced (11). Harth *et al.* (10) measured rate constants for both Ne^+ and CS_2^- formation during collisions between Ne (ns, nd) Rydberg atoms and CS_2 . For large values of the effective principal quantum number ($n^* \geq 25$) they found that the rate constants for formation of long-lived CS_2^- ions were much smaller than those for Ne^+ formation, indicating that CS_2 was indeed capturing the Rydberg electron but that the resulting negative ion was very short-lived. However as n^* was decreased, the rate constant for CS_2^- production increased rapidly, becoming comparable to that for Ne^+ formation for $n^* < 25$. These results provided further evidence that the nascent negative ions could be stabilized by energy transfer with the Rydberg core.

Although these previous studies have provided some insight into the dynamics of CS_2^- formation during RET, the isotope dependence observed for CS_2^- is still not understood. Since it is clear from these studies that energy transfer between the negative ion and the Rydberg core are necessary for production of long-lived CS_2^- ions, we have studied the isotope dependence of CS_2^- formation rates using rubidium Rydberg atoms, which have a core configuration different from that of cesium.

Experimental

The experimental apparatus has been described in detail previously (3,6) and is only briefly described here. Rubidium atoms in a collimated effusive beam ($\sim 240^\circ\text{C}$) were excited to ns and nd Rydberg levels in a field-free region (defined by two parallel mesh grids) by resonant two-photon absorption using the outputs of two independently tunable nitrogen-pumped dye lasers (Moletron). The first laser was fixed at the $5S \rightarrow 5P_{3/2}$ transition (780.2 nm) of atomic Rb while the second laser was tuned to a specific $5P_{3/2} \rightarrow nS$ or nD transition. The excited Rb beam was crossed at 90° with a beam of CS_2 containing naturally occurring isotopic abundances. Two different methods were used to produce the CS_2 beam. A glass capillary array was used to produce an effusive beam (cw) of CS_2 at room temperature. Alternatively, a pulsed nozzle expansion of neat CS_2 was

collimated to produce a pulsed beam of jet-cooled CS_2 . When using the pulsed nozzle (Lasertechnics), the time delay between the opening of the nozzle and the firing of the lasers could be varied in order to sample different regions of the gas pulse. In addition, the pulsed nozzle could be heated up to a temperature of $\sim 75^\circ\text{C}$. After the lasers were fired, collisions were allowed to occur for a specified time (typically 0.5 - 10 μs) after which a voltage pulse was applied to one of the grids to accelerate the positive or negative ions present in the collision zone into the drift tube of a 1.5 meter time-of-flight mass spectrometer (TOFMS). At the exit of the TOFMS the ions were further accelerated into a dual microchannelplate multiplier and detected. The output signal from the multiplier was averaged over several hundred laser pulses and recorded using a 200 MHz transient digitizer (DSP Technology) controlled by a laboratory computer (Compaq 286 DeskPro) via a CAMAC interface. Negative ion isotope ratios were determined by integrating each peak in the mass spectrum and determining the ratios of the peak areas.

Safety Considerations. Three major safety concerns were present during these experiments: (a) handling of alkali metals, (b) handling of carbon disulfide, and (c) hazardous radiation from the lasers. Special precautions were taken to ensure that these hazards produced a minimum risk to personnel. In addition, standard laboratory safety practices (e.g., wearing approved safety glasses) were followed.

Alkali metals are extremely reactive and even explosive when exposed to water or moist air. In addition to safety glasses, a full face shield and appropriate gloves were worn while handling the metals. The alkali reagents were purchased and stored in sealed glass ampoules with break seals. Loading the alkali oven consisted of breaking the glass ampoule, placing the entire ampoule into the oven chamber, and sealing the oven chamber flange. Whenever possible, this operation was conducted in a glove bag under a dry nitrogen or argon atmosphere in a location well removed from any flammable materials. Once the oven flange was sealed the oven was placed in the vacuum apparatus as quickly as possible and pumped down. Cleaning the alkali oven after use consisted of slowly reacting any remaining alkali with small amounts of water until fully deactivated, then washing and rinsing the oven. This operation was conducted behind a plexiglass shield in a fume hood which removed toxic vapors emitted during the deactivation.

Carbon disulfide is a highly flammable and poisonous liquid with a large vapor pressure (300 Torr at 20°C). It can be easily inhaled or absorbed through the skin if proper precautions are not taken. In order to introduce CS_2 into the vacuum apparatus it was first transferred from the reagent bottle into a glass bulb with a vacuum valve attached. This transfer was conducted in a fume hood (located away from any ignition sources) while wearing appropriate protective clothing (gloves, lab coat with long sleeves, etc.). Once transferred, the bulb was sealed and attached to a stainless steel vacuum manifold on the apparatus. The vacuum manifold was regularly checked for leaks. The glass bulb was enclosed in wire mesh cage to protect against external shock (and glass fragments in case of explosion or implosion).

The laser radiation used for exciting the alkali atoms presented a potential risk for eye injury. All laser operations were performed within the guidelines set forth in the current *American National Standard for the Safe Use of Lasers* (26). Whenever possible, the laser beams were contained within appropriate enclosures (e.g., tubes) to prevent inadvertent exposure to the laser radiation. In addition, appropriate laser goggles were worn during laser operation. Many laser dyes are known or suspected carcinogens and were handled accordingly. In addition, many solvents used for dye solutions are toxic or flammable or both and were handled according to standard laboratory safety practices. The preparation of laser dye solutions was performed in a fume hood while wearing appropriate protective clothing (gloves, etc.).

Results

Typical negative ion mass spectra obtained following collisions of Rb (nd) Rydberg atoms with a room temperature effusive beam of CS_2 are shown in Figure 1. As was found previously for Cs Rydberg atoms (3), the ratio of the intensity for mass 78 ions to that for mass 76 ions is dependent upon the initial state of the Rydberg atom. The concentrations of the various CS_2 isotopes in the reagent gas are in the same proportion as their natural abundances. (This was verified by an independent mass spectral analysis of the reagent sample). Therefore, ratios of negative ion intensities which differ from the natural abundance ratio indicate that the rate constants for CS_2^- formation are different for CS_2 molecules of different isotopic composition. Figure 2 shows the negative ion intensity ratio, $R = I(\text{mass } 78)/I(\text{mass } 76)$ as a function of the effective

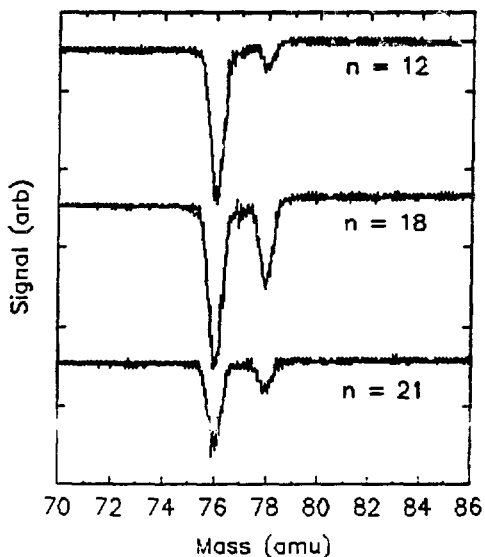


Figure 1. Negative ion mass spectra obtained for several nd states of Rb. The plots have been shifted vertically for clarity.

principal quantum number, n^* , for both the ns and nd states of Rb. For $10 < n^* < 23$, R deviates significantly from the value expected based upon the natural abundances of isotopes with these masses ($R = 0.089$). For $n^* \approx 17$, the rate constant for production of mass 78 ions is ~ 4.8 times larger than that for production of mass 76 ions. The results shown in Figure 2 for Rb are nearly identical with our previous results for Cs (3), which were also obtained for a room-temperature effusive beam of CS_2 .

As we mentioned in our previous report (3), the negative ion isotope ratios observed when CS_2 was expanded in a nozzle jet depended strongly upon the jet expansion conditions, suggesting that the isotope effect may depend upon either the internal temperature of the CS_2 or upon the collision energy (or both). We have previously demonstrated (6) that rate constants for negative ion formation during RET are sensitive to the collision energy for $\text{Cs}(n,l) - \text{SF}_6$ collisions. Our nozzle jet experiments with CS_2 were complicated, however, by the presence of CS_2 clusters in the jet which also capture Rydberg electrons to produce negative ions (27). Figures 3 and 4 show negative ion mass spectra obtained for the $18D$ state of Rb with a nozzle jet expansion of neat CS_2 and with different delay times, t_d , between the opening of the nozzle and the firing of the lasers used to produce the Rydberg atoms. By varying t_d it was possible to sample regions of the jet expansion which had undergone differing amounts of collisional relaxation and cooling. Shorter delay times (Figure 4) sample the leading edge of the jet pulse where fewer collisions (and therefore less cooling and clustering) have occurred during the expansion. As can be seen in the

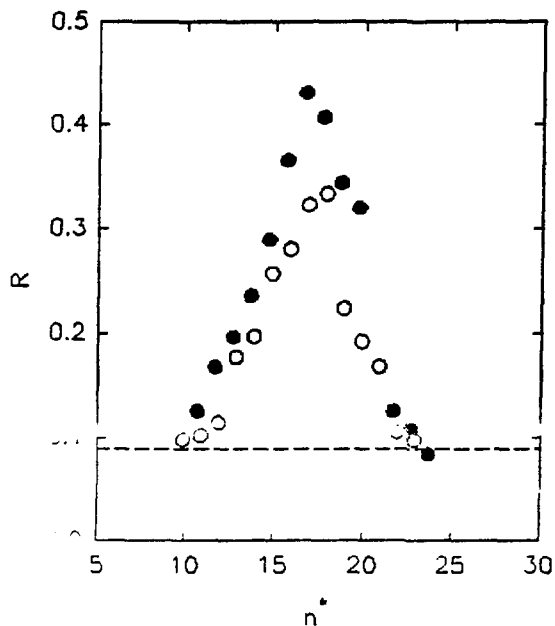


Figure 2. Negative ion intensity ratio, $R = I(\text{mass } 78)/I(\text{mass } 76)$, vs. n^* for the ns (\circ) and nd (\bullet) states of Rb. The dashed line shows the ratio expected based upon natural abundances.

figures, the number of cluster ions observed depended strongly upon which region of the jet was being probed. It is interesting to note that the isotope ratio, R , also depended upon t_d : $R = 0.68$ and 0.47 for $t_d = 210 \mu\text{s}$ and $350 \mu\text{s}$, respectively. However, the fact that dissociative attachment to clusters of CS_2

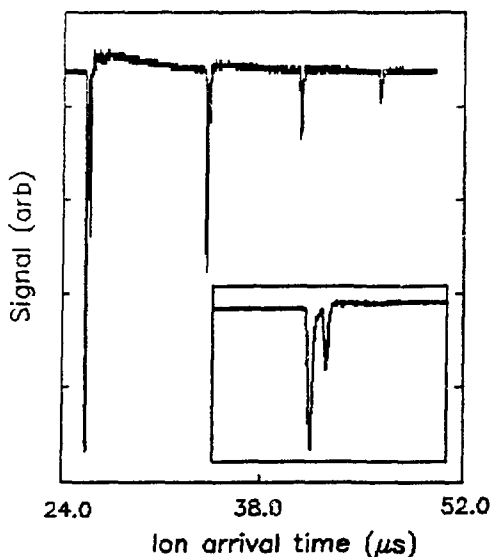


Figure 3. Negative ion mass spectrum obtained for the 18D state of Rb with a $350 \mu\text{s}$ delay between the opening of the pulsed nozzle and the firing of the lasers used to excite Rb. Inset shows an expanded view near region of mass 76 and mass 78 peaks.

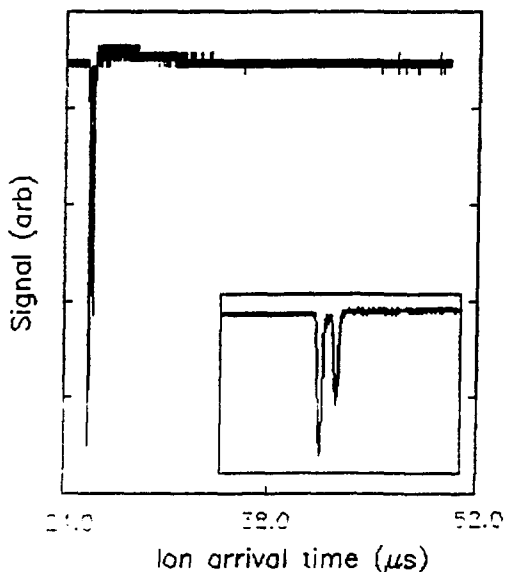


Figure 4. Negative ion mass spectrum obtained for the 18D state of Rb with a $210 \mu\text{s}$ delay between the opening of the pulsed nozzle and the firing of the lasers used to excite Rb. Inset shows an expanded view near region of mass 76 and mass 78 peaks.

may also lead to CS_2^- formation precludes any definitive correlation of R with the internal temperature of CS_2 . We cannot distinguish between CS_2^- ions which have been formed by dissociative attachment to clusters and those formed directly by attachment to CS_2 .

Negative ion mass spectra were also obtained for different temperatures of the pulsed nozzle, T_n , while keeping t_d fixed ($\sim 250 \mu\text{s}$) such that no cluster ions were observed. Under these conditions, R was found to increase linearly from 0.55 at $T_n = 25^\circ\text{C}$ to 0.88 at $T_n = 70^\circ\text{C}$ for the 18D state of Rb. Figure 5 shows a plot of R vs. n^* for $T_n = 70^\circ\text{C}$. Qualitatively, the results are similar to those obtained for a room temperature effusive beam of CS_2 . However, the maximum deviation of R from the natural abundance ratio is much larger for the 70°C jet source than for the room temperature effusive source, reaching a maximum of 0.94 for $n^* \approx 18$. The rate constant for production of mass 78 ions is thus ~ 10.5 times larger than that for production of mass 76 ions under these conditions. Comparison of Figures 2 and 5 suggests that, indeed, R is dependent upon either the collision energy or the internal energy of CS_2 . Unfortunately, direct measurements of the velocity distributions or the rotational and vibrational state populations of molecules in the jet were not possible at the time of these measurements. Such measurements will be necessary before any definitive conclusions can be reached about the effects of collision energy or CS_2 internal energies on the negative ion isotope ratios. Another test would be to vary the temperature of the effusive source, which produces a beam of molecules with well-characterized (Boltzmann) distributions of rotational, vibrational, and translational energies. However such a study was not possible with the effusive source used in these experiments.

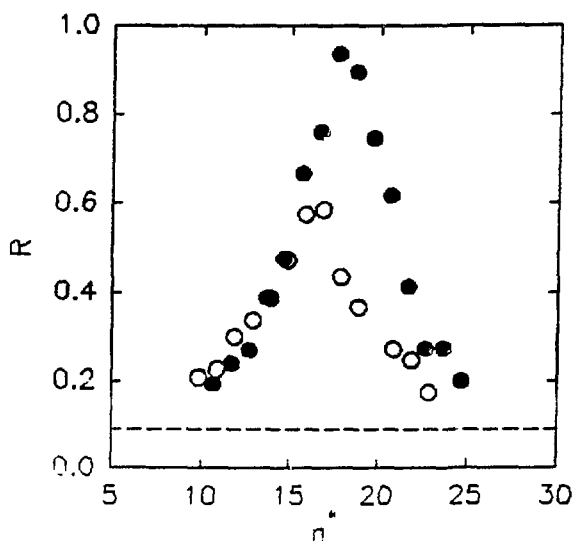


Figure 5. R vs. n^* for the ns (\circ) and nd (\bullet) states of Rb with CS_2 expanded from a 70°C pulsed nozzle. The dashed line shows the ratio expected based upon natural abundances.

Discussion

The fact that stable CS_2^- ions can be produced by Rydberg electron capture but not by free electron capture is easily rationalized by invoking energy transfer between the nascent (short-lived) negative ion and the Rydberg core. The origin of the isotope dependence for the rates of CS_2^- formation, however, remains a mystery. Although there are twenty stable isotopes of CS_2 , our sensitivity limits us to observations of the two most abundant isotopes: $^{32}\text{S}^{12}\text{C}^{32}\text{S}$ (89.25% natural abundance) at mass 76 and $^{32}\text{S}^{12}\text{C}^{34}\text{S}$ (7.93% natural abundance) at mass 78. Two additional mass 78 isotopes exist ($^{33}\text{S}^{12}\text{C}^{33}\text{S}$, <0.01% and $^{32}\text{S}^{13}\text{C}^{33}\text{S}$, 0.02%) but we assume, based upon the natural abundances, that $^{32}\text{S}^{12}\text{C}^{34}\text{S}$ is the only significant contributor to the signal at mass 78.

Isotope effects for *nonionizing* processes involving Rydberg atoms have been previously reported (28,29). Gallagher *et al.* (28) found that cross sections for quenching of the ns states of Na during collisions with CH_4 and CD_4 were strongly dependent upon n and that the n -dependence was different for the two molecules. The quenching cross sections were greatly enhanced by resonant electronic-to-vibrational energy transfer when the energy difference between two vibrational levels of the molecule was nearly equal to the energy difference between two electronic levels of Na. Since the vibrational level spacings for CH_4 and CD_4 are different due to the isotopic substitution, the resonance energies for the two molecules are matched by different $nl - n'l'$ transitions of Na. Similar results were reported by Petitjean *et al.* (29) for $\text{Rb}(ns, nd) + \text{NH}_3, \text{ND}_3$ collisions. While these studies demonstrated isotope effects for deexcitation (quenching) of Rydberg states, it is feasible that such effects may also occur for excitation (including ionization) of Rydberg atoms, whereby molecular rotational or vibrational energy is transferred to electronic energy of the atom. However, Kalamarides *et al.* (11), based upon measurements of n -changing cross sections for $\text{K}(nd)\text{-CS}_2$ collisions, concluded that transfer of molecular vibrational or rotational energy was insignificant for these collisions. Nevertheless it is quite interesting to note that, for $n^* \approx 17$ (where we observed the largest isotope effect), the electron binding energy for Rb ($\sim 380 \text{ cm}^{-1}$) is very nearly equal to one quantum of energy for the bending vibration for CS_2 : $\omega_2 = 395.99 \text{ cm}^{-1}$ and 395.08 cm^{-1} for $^{32}\text{S}^{12}\text{C}^{32}\text{S}$ and $^{32}\text{S}^{12}\text{C}^{34}\text{S}$, respectively (30). The total cross section for CS_2^- formation also peaks near $n^* \approx 17$ (3, 10). Since the ground state of CS_2 is linear and the ground state of CS_2^- is bent, it seems likely that the bending vibration may play an important role in the electron capture process. However, due to the fact that the bending vibrational frequencies of the two isotopes are nearly equal, it seems unlikely that a resonant energy transfer mechanism involving the bending mode would produce the large isotope effect we observe.

While chemical isotope effects in general are related to the mass of a particle through its effect on the Hamiltonian for the system (kinetic isotope effect), several examples are known of isotope effects which arise due to parity or symmetry constraints and are not directly correlated with the mass difference of the isotopes. Several examples of such isotope effects are discussed elsewhere

in this volume. Valentini (31) has recently shown that such parity and symmetry constraints may result in isotope-dependent selection rules for nonadiabatic transitions involving linear molecules which contain atoms with isotopes of zero nuclear spin located in two equivalent positions (e.g., O₂, CO₂, CS₂). Specifically, he showed that when such molecules possess a Σ electronic state which is coupled via a nonadiabatic transition (curve crossing) with a state of nonzero electronic angular momentum (e.g., Π or Δ), the nonadiabatic transition rate will be twice as great for non-symmetric molecules (different isotopes in equivalent positions) than for symmetric molecules (identical isotopes in equivalent positions). The basis for this isotope dependence lies in the selection rules associated with the parity of the rotational wave functions of the molecule (31). For the Σ state of the symmetric molecule, half of the rotational levels are missing due to the fact that their wave functions do not possess the required symmetry with respect to interchange of the identical boson nuclei. In contrast, all rotational states are allowed for the Σ state of the non-symmetric molecule and for the non- Σ states of both the symmetric and the non-symmetric molecules. The dynamical effects of these symmetry-related selection rules were elegantly demonstrated by Valentini *et al.* (31,32) for the photodissociation of ozone. Similar selection rules may apply to collisions of Rydberg atoms with CS₂.

For the $^1\Sigma^+$ ground state of CS₂, only even-J rotational states are allowed for the $^{32}\text{S}^{12}\text{C}^{32}\text{S}$ isotope whereas all J values are allowed for $^{32}\text{S}^{12}\text{C}^{34}\text{S}$. In its linear configuration, the ground state of the CS₂⁻ ion has Π_u electronic symmetry with all J values allowed for both $^{32}\text{S}^{12}\text{C}^{32}\text{S}^-$ and $^{32}\text{S}^{12}\text{C}^{34}\text{S}^-$. During a collision with a Rydberg atom, the rates for nonadiabatic transitions between states correlating with the neutral and ionic states of the CS₂ molecule may therefore be isotope-dependent. However, the Rydberg atom-CS₂ system is quite complex, with a number of intersecting potential energy surfaces. As a result, the system is difficult to model, especially when the vibrational motion of the molecule is considered. It is therefore not clear at present if symmetry-related dynamical constraints can account for the large isotope dependence observed for the rates of CS₂⁻ formation.

More than likely, several different factors are contributing to the isotope effect. As can be seen in Figures 2 and 5 and in Figure 1 of reference (3), the values of the negative ion isotope ratio, R, are consistently smaller for the *ns* states of the alkali atom compared to the *nd* states. This observation suggests that the symmetry of the Rydberg atom states must also be considered and that conservation of angular momentum for the total system may present dynamical constraints which are isotope-dependent. Further experimental and theoretical studies are necessary to provide more insight into the dynamics of these interesting reactions. Experiments with isotopically enriched CS₂ (especially of the symmetric and non-symmetric heavier isotopes) are currently being planned in our group. Also planned are experiments using stimulated emission pumping to prepare vibrationally and rotationally state-selected CS₂ molecules. Methods for determining the translational energy and state populations of CS₂ in the jet beam are currently being explored.

Acknowledgments

This research was sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Useful discussions with Professors R.F. Curl, Jr. and J.J. Valentini are gratefully acknowledged.

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