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Inelastic electron–dipole-molecule scattering at sub-milli-electron-volt energies: CH₃I and CH₂Br₂

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Studies of Rydberg-atom destruction in collisions with the polar targets CH_3I and CH_2Br_2 for values of principal quantum number n in the range 100–400 are reported. Analysis of the data using the essentially-free-electron model suggests that, for ultralow electron energies (~ 80 μeV to 1 meV), the cross section $\sigma(\varepsilon)$ for rotationally inelastic scattering of electrons by a polar target varies approximately as $1/\varepsilon$, where ε is the electron energy. The Born approximation does not predict such behavior at very low collision energies, and possible reasons for this discrepancy are discussed.

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For sufficiently large values of principal quantum number n, collisions involving Rydberg atoms can be described using the essentially-free-electron model, which assumes that the separation between the excited Rydberg electron and its associated core ion is so large that both do not interact simultaneously with a target particle [1]. Thus, because the average kinetic energy of the Rydberg electron ($\sim 13.6/n^2$ eV) is very small, studies of Rydberg-atom collision processes that are dominated by the binary Rydberg-electron–target interaction can provide information on electron/molecule scattering at subthermal electron energies. In the present work electron–polar-molecule scattering is investigated at ultralow energies (~ 1.4 meV to 80 μeV) by measuring rate constants for destruction of potassium Rydberg atoms with $n \sim 100$–400 in collisions with CH_3I and CH_2Br_2. Earlier work [2–4] at lower n ($n \sim 30$) has demonstrated that rotational energy transfer in collisions with polar molecules, which results predominantly from dipole-allowed rotational transitions, can lead to ionization and to population of localized groups of higher n states. However, for very large values of n, the Rydberg electron is sufficiently weakly bound that the majority of such ro-

tational transitions will, for a room-temperature (300-K) rotational distribution, lead directly to ionization. Assuming that Rydberg-atom destruction results solely from rotational energy transfer in a binary Rydberg-electron–target encounter, analysis of the present data suggests that, at ultralow electron energies, the cross section $\sigma_e(\varepsilon)$ for rotationally inelastic electron–polar-
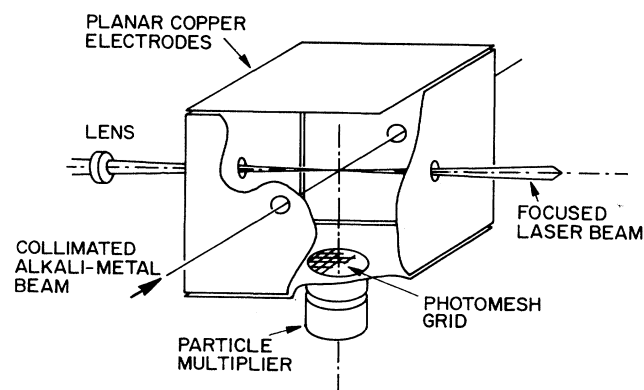

FIG. 1. Schematic diagram of the apparatus.

molecule scattering varies approximately as $1/\varepsilon$, where ε is the electron energy. The Born approximation does not predict such behavior at ultralow collision energies [5] and possible reasons for this discrepancy are discussed.

The present apparatus is shown schematically in Fig. 1 and has been described in detail elsewhere [6]. Briefly, potassium atoms contained in a thermal-energy (600-K) beam are photoexcited to a selected np state using a frequency-doubled Coherent CR699-21 rhodamine 6G dye laser. The output of the laser is formed into a series of pulses of ~ 2 μsec duration with a pulse repetition frequency of $\sim 5 - 10$ kHz using an acousto-optic modulator. Excitation occurs, in zero electric field and (typically) in the presence of target gas, near the center of an interaction region defined by three pairs of planar copper electrodes. Following excitation, collisions are allowed to occur for a predetermined time whereupon the number and/or excited-state distribution of Rydberg atoms remaining in the interaction region are determined using field ionization. A voltage ramp is applied to the lower electrode and the electrons resulting from field ionization are detected by a Johnston multiplier.

Rydberg-atom collisions with polar targets lead to state changing and to ionization [2–4]. The Rydberg-atom pop.:lation in the interaction region thus comprises both parent np states and the products of state-changing reactions, which, as will be justified later, can be treated as a single "mixed" population [2]. Assuming that collisional ionization is the only process contributing to Rydberg-atom destruction, the time evolution of the parent and mixed populations $N_0(t)$ and $N_1(t)$, respectively, following each laser pulse will be described by the rate equations

$$\frac{dN_0(t)}{dt} = -\rho(k_l + k_{i0})N_0(t) \ , \tag{1}$$

$$\frac{dN_1(t)}{dt} = -\rho k_{i1}N_1(t) + \rho k_l N_0(t) \ , \tag{2}$$

where ρ is the target-gas number density (measured using an ionization gauge calibrated against a capacitance manometer), k_l is the rate constant for state changing,
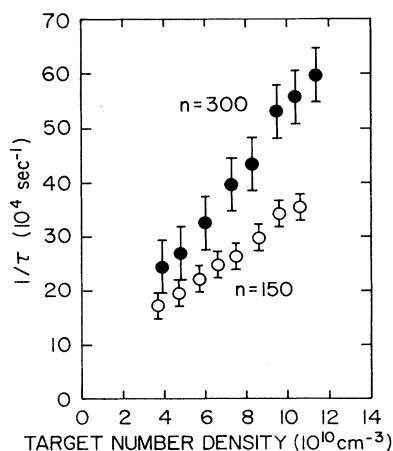

FIG. 2. The measured decay rate $1/\tau$ as a function of target-gas density ρ for collisions with CH_2Br_2.
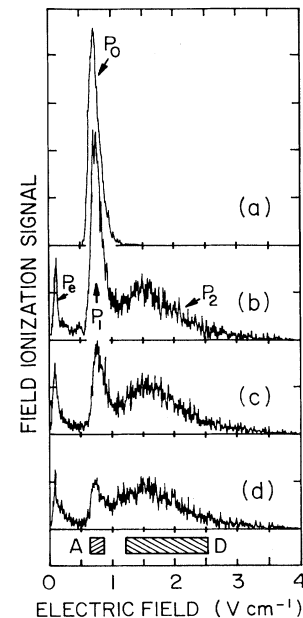

FIG. 3. SFI spectra pertaining to $K(150p)$-CH_3I collisions. (a) SFI spectrum obtained with no target gas present. (b)–(d) SFI spectra obtained after allowing collisions to occur for 2, 4, and 6 μsec, respectively, following laser excitation. The horizontal bars beneath the data indicate the range of field strengths over which adiabatic (A) and diabatic (D) ionization of states with $n = 150$ is expected.

and k_{i0} and k_{i1} are the rate constants for collisional ionization of parent atoms and the mixed population, respectively. Solution of these equations provides the time evolution of the total Rydberg atom population $N(t)$

$$N(t) = N_0(t) + N_1(t)$$

$$= N_0(0) \left\{ \frac{k_{i0} - k_{i1}}{k_l + k_{i0} - k_{i1}} \right\} e^{-\rho(k_l + k_{i0})t}$$

$$+ \left\{ \frac{k_l N_0(0)}{k_l + k_{i0} - k_{i1}} + N_1(0) \right\} e^{-\rho k_{i1}t} \ . \tag{3}$$

If, as will be shown, $k_l + k_{i0} > k_{i1}$, then for relatively large values of ρt, as used in the present work, the second term in Eq. (3) dominates and $N(t)$ varies as

$$N(t) \sim e^{-\rho k_{i1}t} \equiv e^{-t/\tau} \ , \tag{4}$$

where $1/\tau (= \rho k_{i1})$ is the decay rate. Measurements confirmed that $N(t)$ was well described by a single exponential and that, as illustrated in Fig. 2 for CH_2Br_2, the decay rate increased linearly with increasing ρ.

State-changing was investigated using selective field ionization (SFI) in which the electron signal resulting from field ionization is measured as a function of applied field. Since atoms in different states ionize at different field strengths, analysis of SFI data can provide information on the distribution of excited states present at the time of application of the SFI voltage ramp [2,3]. SFI data pertaining to $K(150p)$-CH_3I collisions are presented in Fig. 3, together with the ranges of field strength (in-

ferred from earlier measurements [7]) over which diabatic and adiabatic ionization of atoms in states with $n \sim 150$ is expected. [Low (high) $|m_l|$ states tend to ionize adiabatically (diabatically).] In the absence of target gas, the SFI spectrum comprises a single sharp peak, P_0, that results from adiabatic ionization of the parent state. Collisions result in the growth of a broad, higher-field SFI feature, P_2, that can be attributed to diabatic ionization of states with a broad, possibly statistical, distribution of $l, |m_l|$ values produced through quasielastic state-changing reactions [1,8]. The small peak P_e at very low field strengths results from electrons produced through collisional ionization that remain in the interaction region when the voltage ramp is applied. Collisional ionization also occurs during the voltage ramp and produces a small background. No significant signal attributable to SFI was observed at field strengths characteristic of ionization of states with n much greater than 150, indicating that collisions populate states in, at most, a very restricted range of n manifolds adjacent to the parent level. Since single state-changing collisions lead directly to large changes in $l, |m_l|$ but not in n, it is reasonable to assume that subsequent collisions will not, on average, significantly alter the state-changed population distribution allowing the state-changed atoms to be considered as a single mixed population.

Analysis of the growth of the P_2 feature at low target-gas densities showed that the rate constant k_l for state changing is large, $\sim 5 \times 10^{-6}$ cm^3 sec^{-1}. (Similar measurements with CH_2Br_2 yielded $k_l \sim 3 \times 10^{-6}$ cm^3 sec^{-1}.) SFI could not be used to study state changing at $n \gtrsim 200$ because both parent and product states ionized diabatically and were not readily distinguishable. Analysis of the time development of the feature P_1, which results primarily from ionization of parent $150p$ states, indicated that the rate constant for parent-state depopulation, i.e., $k_l + k_{i0}$, is very large $\sim 8 \times 10^{-6}$ cm^3 sec^{-1}, suggesting a rate constant $k_{i0} \sim 3 \times 10^{-6}$ cm^3 sec^{-1} for parent-state collisional ionization. (The corresponding values for CH_2Br_2 are $k_l + k_{i0} \sim 9 \times 10^{-6}$ cm^3 sec^{-1} and $k_{i0} \sim 6 \times 10^{-6}$ cm^3 sec^{-1}.)

The measured rate constants k_{i1} for collisional ionization of the mixed population are presented in Fig. 4. The observed linear increase in the rate constant with n contrasts the behavior noted earlier in studies with the nonpolar attaching targets SF_6 and CCl_4 [6]. For these targets the rate constants for collisional ionization, which result primarily from capture of the Rydberg electron by the target molecule, are essentially independent of n over the present range. Such behavior is characteristic of an s-wave capture process [9] and has been observed with a wide variety of attaching targets [10]. Both CH_3I and CH_2Br_2 capture low-energy electrons, and interpolation of the present data to low n (where ionization through rotational energy transfer becomes less likely) suggests that the rate constant for such reactions will be $\sim 5 \times 10^{-7}$ cm^3 sec^{-1}, which is comparable to those observed with other attaching targets [10].

Simple s-wave capture, however, cannot account for the observed n dependence in the measured rate con-
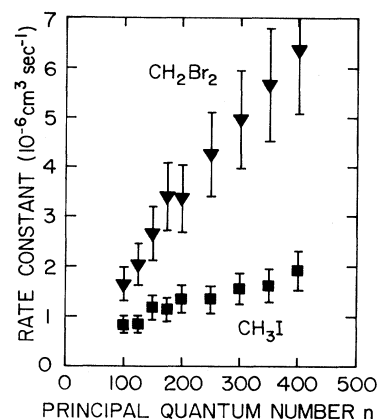

FIG. 4. Rate constants k_{i1} for collisional ionization of a mixed population as a function of n.

stants k_{i1}. One possible explanation is that as n increases, and the binding energy of the Rydberg electron decreases, the energy transfer associated with quasielastic scattering of the Rydberg electron by the target molecule [8] becomes sufficient to lead directly to ionization. However, tests undertaken using CO_2 (electron-CO_2 scattering is characterized by an unusually large momentum transfer cross section at low energies) failed to provide any evidence of such direct collisional ionization at $n = 250$. Further, energy transfer accompanying quasielastic electron scattering would be expected to populate a broad distribution of higher n states, and these are not observed in the SFI data.

It is thus reasonable to assume that the n dependence evident in Fig. 4 arises from an n dependence in the contribution to the total collisional ionization rate that results from rotational energy transfer reactions of the type [11]

$$K(n) + CH_3 I(J,K) \rightarrow K^+ + CH_3 I(J-1,K) + e^- . \quad (5)$$

The observed behavior could then be explained if, as n increases, the number of rotational transitions that contribute to ionization increases. This explanation can be discounted because calculations show that for the present targets more than 80% of dipole-allowed transitions will, for a room-temperature rotational distribution, lead directly to ionization, even at $n = 150$ [12,13]. Also, preliminary studies using HF, which has a very simple rotational structure and for which all rotational transitions result in ionization for $n \gtrsim 53$, show a linear increase in k_{i1} with n over the present range.

According to the essentially-free-electron model, the rate constant k'_{i1} associated specifically with ionization through rotational energy transfer [Eq. (5)] should equal that for rotational deexcitation of the target molecule by free electrons having the same velocity distribution as the Rydberg electrons, i.e.,

$$k'_{i1} = \int_0^\infty v \sigma_e(v) f(v) dv , \quad (6)$$

where $\sigma_e(v)$ is the cross section for rotationally-inelastic

scattering of free electrons with velocity v, and $f(v)$ is the electron velocity distribution. Expressions for $\sigma_e(v)$ have been derived using the Born approximation [see, for example, Eq. (9) in Ref. [5]] and suggest that, for ultralow electron energies, $\sigma_e(v)$ should scale approximately as $1/v$. Given this form for $\sigma_e(v)$, Eq. (6) would predict that, contrary to the present observations, k'_{i1} should be essentially independent of n over the present range. Instead, the observed linear increase in k'_{i1} with n suggests that $\sigma_e(v)$ varies approximately as $1/v^2$, i.e., $1/\varepsilon$. [In this event, Eq. (6) requires that k'_{i1} be proportional to $\langle 1/v \rangle$, which, in turn, is approximately proportional to n.] A $1/v^2$ dependence of $\sigma_e(v)$ is also consistent with the observation that, for both targets, the rate constants inferred for ionization of the parent $150p$ state are significantly greater than those for ionization of the corresponding l-mixed population, because, for a given n, $\langle 1/v \rangle$ for a p state is significantly larger than for a statistically mixed l distribution.

Given the discrepancy between the present measurements and predictions based on the Born approximation, it is sensible to question the applicability of the essentially-free-electron model. Matsuzawa [1], however, has argued that for values of $n \sim 30$ the criteria for application of this model to collisions involving polar molecules are well satisfied, and that as n increases the Rydberg electron behaves even more like a free electron. Indeed, although the cross sections for electron/dipole scattering ($\sim k'_{i1}/v_{rms}$, where v_{rms} is the root-mean-square Rydberg-electron velocity) derived from the present measurements correspond to relatively large interaction ranges (~ 50–200 Å), these ranges are much smaller than the characteristic atomic radii ($\sim 5 \times 10^3$–8×10^4 Å). It therefore appears reasonable to discuss the present collisions in terms of a binary interaction between the Rydberg electron and target molecule.

The present work thus suggests that the Born approximation does not correctly describe electron/dipole scattering at ultralow electron energies. The scattering conditions are, however, quite unusual in that the electron energies correspond to large de Broglie wavelengths, ~ 330–1300 Å, and that the collision time is comparable to the period of molecular rotation [14]. Difficulties with the Born approximation are, perhaps, not surprising because the collisions are not "weak," i.e., the energy transferred to the electron through rotational deexcitation is substantial, resulting in a large fractional change in its momentum. Also, CH_3I and CH_2Br_2 have sizeable dipole moments (1.62 and 1.43 D, respectively) and while these are insufficient to allow formation of stable dipole-bound negative ions [15] it is, nonetheless, possible that quasibound negative-ion resonances might be important in the scattering. Certainly, experimental and theoretical studies of photodetachment from negative ions in which the products are a free electron and a polar molecule show that the presence of the dipole potential in the exit channel significantly modifies the photodetachment threshold behavior [16].

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