Stimulated-absorption and spontaneous-emission studies of laser-induced dipole-quadrupole collisions

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Observations are made of dipole-quadrupole laser-induced inelastic collisions occurring during the collision of two Ba atoms. Results for both stimulated-absorption and spontaneous-emission experiments using the same collisional configuration are reported for the first time. In both experiments the interaction maximizes at the $R = \infty$ wavelength and has a full-width-at-half-maximum linewidth of ~ 8 cm^{-1}. These results bear on the study of the interatomic potentials for colliding atoms and permit the collisional energy transfer to states hitherto inaccessible to dipole-dipole collisions.

I. INTRODUCTION

The term laser-induced inelastic collision refers to a long-range collision process whereby a laser field is used to induce selective excitation or energy transfer between colliding atomic or molecular species. Conversely, a photon may be radiated during the collision of two excited species resulting in the spontaneous-emission analog of laser-induced interactions, termed radiative collisional fluorescence. These phenomena have attracted considerable experimental and theoretical attention in recent years.[1-17] Initial studies of laser-induced collisions were concerned with dipole-dipole collisional coupling, where one species makes a parity-allowed transition while the other species makes a parity-nonallowed transition. Dipole-dipole interactions have been extensively studied in stimulated absorption and spontaneous emission using a variety of experimental techniques.[3,4,11-14] More recently the higher-order dipole-quadrupole collisional coupling has begun to come under scrutiny.[15,16] In the dipole-quadrupole interaction both of the colliding species make either parity-allowed or parity-nonallowed transitions.

In the present work the laser-induced dipole-quadrupole interaction between two Ba atoms is studied in both stimulated absorption and the reverse spontaneous-emission process. This study is carried out for the first time using the same collision configuration, allowing direct comparison of the necessarily complementary process. The pertinent energy levels for the two colliding Ba atoms used in this study are shown in Fig. 1. The absorption process, described in Sec. II, is represented by the collision scheme

$$\mathrm{Ba}(6s^2\,{}^1S_0) + \mathrm{Ba}(6s^2\,{}^1S_0) + \hbar\omega(4386.5\ \text{Å}) \rightarrow \mathrm{Ba}(5d\,{}^1D_2) + \mathrm{Ba}(5d\,{}^1D_2), \quad (1)$$

where the energy of the absorbed photon equals the sum of the energies of the two Ba($5d\,{}^1D_2$) metastable levels. This process may be viewed as a virtual absorption followed by dipole-quadrupole collision. During the collision of the two Ba ground-state atoms, a photon of energy 22 790 cm^{-1} can be absorbed by one of the Ba atoms resulting in its excitation to a virtual level with $6p\,{}^1P_1^o$ character. While in this virtual level, the $6p\,{}^1P_1^o$-like atom may undergo a long-range dipole-quadrupole collision with a second Ba ground-

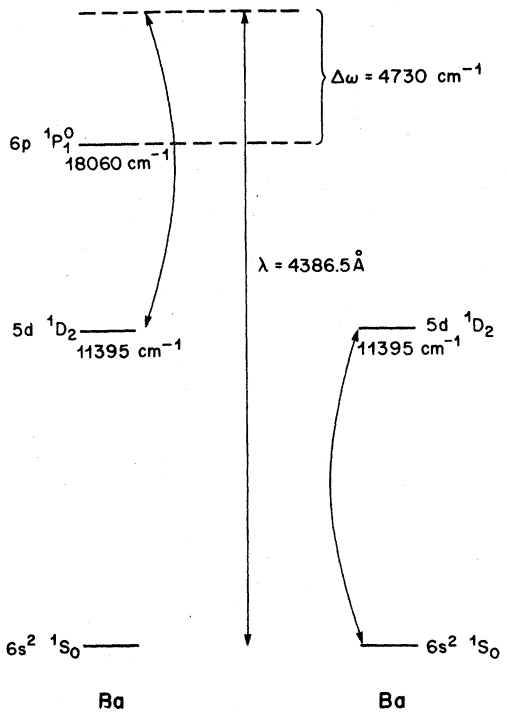

FIG. 1. Energy level diagram for dipole-quadrupole collision between two Ba atoms. The absorption and emission processes maximize for a photon energy equal to the sum of the energies of the two Ba ($5d\,{}^1D_2$) atoms. The curved lines indicate the pathway for the dipole-quadrupole coupling.

state atom resulting in the deexcitation of the first atom to its $5d\,^1D_2$ state, the excitation of the second atom to its $5d\,^1D_2$ state. Section II describes the experimental observation of this process, where optogalvanic detection, recently shown to be a sensitive tool in the study of the dipole-dipole collisions, [13] has been applied for the first time to the study of the higher-order dipole-quadrupole interaction.

The spontaneous-emission process or radiative collisional fluorescence is described in Sec. III and is represented by the spontaneous-emission analog of process (1), namely,

$$\mathrm{Ba}(5d\,^1D_2)+\mathrm{Ba}(5d\,^1D_2) - \mathrm{Ba}(6s^2\,^1S_0)+\mathrm{Ba}(6s^2\,^1S_0)+\hbar\omega(4386.5\ \text{Å}). \quad (2)$$

This process results in the spontaneous radiative deexcitation of both $\mathrm{Ba}(5d\,^1D_2)$ atoms to their ground states with the emission of a photon at the sum of the energies of the two $5d\,^1D_2$ atoms. In a manner completely analogous with the absorption process, the perturbation sequence is modeled as a virtual dipole-quadrupole collision followed by a real emission at 4386.5 Å (all wavelengths given in air). This spontaneous-emission process in Ba is reported here for the first time and represents only the second observation of such dipole-quadrupole emission. [16]

Theoretical considerations indicate that both the absorption process (1) and the emission process (2) should maximize when the energy of the absorbed (radiated) photon is equal to the sum energy of the $\mathrm{Ba}(5d\,^1D_2)$ atoms for infinite separation.[5] As is the case for laser-induced dipole-dipole collisions, the wavelength corresponding to the sum energy is termed the $R=\infty$ wavelength. [2,5] Both experiments reported here confirm this key theoretical prediction. Note that these frequencies do not correspond to any tabulated characteristic frequencies of the isolated atoms.

II. STIMULATED-ABSORPTION EXPERIMENT

The observation of the absorption process (1) was carried out using optogalvanic detection in a discharge containing the Ba vapor. The fractional change F in the steady-state discharge populations due to the absorption of radiation via the dipole-quadrupole collision which results in the optogalvanic effect may be calculated based on simple collision rate arguments and on line center is [13]

$$F=N[\mathrm{Ba}(6s^2\,^1S_0)]\sigma_c(P/A)\overline{V}\tau. \quad (3)$$

Here, $N[\mathrm{Ba}(6s^2\,^1S_0)]$ is the number density of initial ground-state Ba stoms, $\sigma_c(P/A)$ is the laser-induced collision cross section for dipole-quadrupole absorption, P/A is the applied laser power density, $\overline{V}$ is the mean velocity for collision, and τ is the laser pulse length. In the weak field regime the collision cross section may be calculated using the relation [15]

$$\sigma_c(P/A)=\left(\frac{\pi^3}{2\hbar^2\overline{V}^2}\right)\left(\frac{3\mu_1\gamma}{2\rho_0^2}\right)^2\left(\frac{\mu_2 E}{2\hbar\Delta\omega}\right)^2, \quad (4)$$

where μ_1 and μ_2 are the $\mathrm{Ba}(6s^2\,^1S_0-6p\,^1P_1^o)$ and Ba $(6p\,^1P_1^o-5d\,^1D_2)$ dipole matrix elements, respectively, γ is the $\mathrm{Ba}(6s^2\,^1S_0-5d\,^1D_2)$ quadrupole matrix element, E is the applied laser field strength, $\Delta\omega$ is the virtual detuning, and ρ_0 is the dephasing or Weisskopf radius. At our operating conditions, one finds $\mu_1=7.9\times10^{-18}$ esu cm, $\mu_2=4.2\times10^{-18}$ esu cm, $\gamma=2.7\times10^{-26}$ esu cm^2 (Ref. 15), $\overline{V}=5.8\times10^4$ cm/sec, $\Delta\omega=4730$ cm^{-1}, and as an estimate $\rho_0\simeq10$ Å; such that the calculated collision cross section for absorption is $\sigma_c=1.8\times10^{-25}(P/A)^{-1}$cm^2. Note that for low incident flux, $\sigma_c(P/A)$ is proportional to P/A; hence the fractional change F in the steady-state discharge populations is linear in the applied laser power density.

The experimental apparatus used to detect the laser-induced collision is shown in Fig. 2 and was similar to the apparatus used in the dipole-dipole collision studies. [13] The Ba metal was contained in a metal vapor oven with a 10 cm-long hot zone constructed from an Inconel outer tube with a tantalum liner sleeve to resist attack by the hot Ba vapor. Two longitudinal, parallel molybdenum ribbons were used as discharge electrodes. These ribbons were supported inside the oven by means of insulated stainless steel pins and were pulled taut by two springs in order to prevent sagging or warping as the oven was heated. A constriction consisting of a sharp point on one electrode and a flat, raised portion on the other electrode was added in the center of the hot zone in order to confine the discharge to the center of the hot zone in the region of high Ba vapor density.

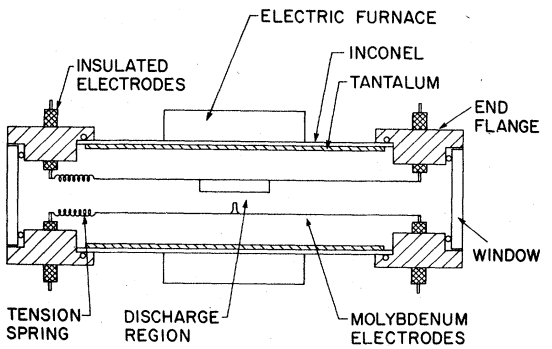

FIG. 2. Configuration of the metal vapor cell used for optogalvanic detection.

The separation of the electrodes in the center of the cell was typically 1 mm. The transient change in the discharge impedance due to the absorption of the pulsed laser radiation at 4386 Å via the dipole-quadrupole collision was measured using a boxcar integrator across a ballast resistor placed in series with the discharge. The resulting signal was plotted using an XY chart recorder.

The laser pump radiation in the vicinity of 4386 Å was generated using the third harmonic of a Q-switched Nd:YAG laser to pump a coumarin 450 dye laser. Approximately 250 μJ in a 7 nsec long pulse at 4386 Å was generated and focused to an area of 1.6×10^{-3} cm^2 between the constricted zone of the electrodes. The metal vapor cell was operated at a temperature of 1100 °C, providing a Ba vapor density of about 9.0×10^{16} atoms/cm^3, as determined by the resonance line curve of growth method. A stable Ba discharge was achieved with a 500-Ω ballast resistor at a 17-V potential with a current of ~7 mA. A He buffer-gas pressure of 35 Torr was chosen in order to damp plasma oscillations in the discharge and also to prevent the Ba vapor from condensing on the cold cell windows.

The experimentally measured absorption profile for process (1) in Ba-Ba is shown in Fig. 3. To within an experimental uncertainty of 0.5 Å, the absorption maximum occurs at the predicted $R=\infty$ wavelength of 4386.5 Å. The dipole-quadrupole collision has a measured full width at half maximum (FWHM) of 7 cm^{-1} and a slight blue asymmetry. The sharp absorption lines at 4383.7 Å and 4389.0 Å correspond to tabulated Fe transitions [18] and the line at 4384.3 Å corresponds to a tabulated Ca transition. [18] These metals are trace impurities present in the Ba metal and become visible in absorption spectra in the discharge environment. The striking difference between the line shape and width of real atomic lines as compared to the collisional absorption is apparent from these data. The Fe and Ca absorptions remained unchanged as the incident laser intensity was lowered by a factor of 3, indicating, as expected, saturation of these dipole allowed atomic transitions. The dipole-quadrupole absorption magnitude was found to vary linearly as the incident flux was lowered a factor of 3, consistent with theoretical considerations for the weak field regime. [5]

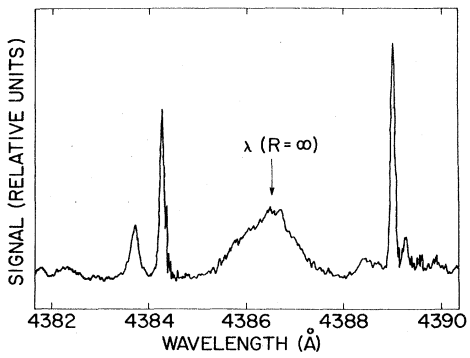

FIG. 3. Observed Ba-Ba dipole-quadrupole absorption at 4386.5 Å. The narrow absorption features at 4383.7 Å and 4389.0 Å correspond to tabulated Fe transitions while the 4384.3 Å feature corresponds to a tabulated Ca transition.

The fractional change F in the steady-state discharge populations due to the dipole-quadrupole collision measured in Fig. 3 can be calculated using Eq. (3). Based on the calculated $\sigma_c = 1.8\times10^{-25}(P/A)^{-1}$cm^2, the peak absorption at 4386.5 Å corresponds to a calculated fractional change of 1.5×10^{-4}. This fractional change is of the same order of magnitude as that previously observed for dipole-dipole collisions in Ba vapor. [13]

III. SPONTANEOUS-EMISSION EXPERIMENT

The radiative emission analog [Eq. (2)] of the absorption study was carried out by observing the spontaneous emission at $\lambda(R=\infty)=4386.5$ Å resulting from the dipole-quadrupole collision between two Ba($5d\,^1D_2$) atoms. Pumping of the Ba($5d\,^1D_2$) level was obtained through stimulated Raman scattering of 3547 Å radiation in the Ba vapor itself. The output of a Q-switched Nd:YAG laser was first frequency doubled and then summed with the fundamental in successive KD*P crystals to generate the third harmonic at 3547 Å. Approximately 12 mJ of 3547 Å radiation in a 7 nsec long pulse was focused to an area of 1.1×10^{-3} cm^2 over 6 cm in the center of the metal vapor cell. Strong stimulated Raman scattering at the first Stokes frequency (5955 Å) was observed. The metal vapor cell, described in detail elsewhere, [17] was constructed from refractory materials and utilized a platinum 60%–rhodium 40% heater to permit high temperature operation. Typically the cell was run at 1300 °C providing a Ba vapor density of about 3.0×10^{17} atoms/cm^3. Argon buffer gas was used to prevent metal vapor condensation on the cold cell windows. Fluorescence from the cell was collected, spatially filtered, and imaged into the detection system consisting of a scanning 0.85 m spectrometer with a resolution of about 0.2 Å and an RCA C31034A photomultiplier tube.

The population present in the initial Ba($5d\,^1D_2$) level was estimated by direct measurement of the energy present at the first stokes (5955 Å) due to

the stimulated Raman scattering of the 3547 Å pump radiation. Based on a measured total energy of ~200 μJ per pulse at 5955 Å, the excited state Ba($5d\,^1D_2$) number density is estimated to be 9.1×10^{16} atoms/cm^3. No significant coherent four-wave or higher-order Raman processes were observed at these operating conditions.

Figure 4 shows the relative magnitude of the dipole-quadrupole spontaneous emission as a function of wavelength. The collisional fluorescence has a maximum at the predicted $R=\infty$ wavelength of 4386.5 Å with a FWHM of 8 cm^{-1}. A slight asymmetry toward shorter wavelength is apparent, in agreement with the absorption data of Fig. 3. The plot of Fig. 4 was taken with 50 Torr of Ar buffer gas; additional data taken with 250 Torr of buffer gas yielded approximately constant magnitude and width for the radiative collisional emission. Note that the sharp atomic emission lines due to Fe and Ca which were observed in the discharge environment (Fig. 3) are no longer present.

The measured magnitude of the radiative collisional emission may be related to a physical cross section for collisional deexcitation by spontaneous emission σ_s. The signal strength integrated over the emission bandwidth is then equal to [11,16]

$$\{N[\mathrm{Ba}(5d\,^1D_2)]\}^2\sigma_s\bar{V}\tau V_0\eta\xi\,, \tag{5}$$

where $N[\mathrm{Ba}(5d\,^1D_2)]$ is the initial storage density, $\bar{V}$ is the mean velocity for collision, τ is the effective radiating time, V_0 is the effective radiating volume, η is the ratio of detected to generated photons, and ξ is related to the photomultiplier responsivity (for the particular measurement electronics used). The typical emission bandwidth integrated signal as observed on an oscilloscope was ~3 mV/pulse. At our operating conditions, $N[\mathrm{Ba}(5d\,^1D_2)]=9.1\times10^{16}$ atoms/cm^3, $\bar{V}=6.2\times10^4$ cm/sec, $\tau\simeq100$ nsec, $V_0=6.6\times10^{-3}$ cm^3, $\eta=3.1\times10^{-5}$, and $\xi\simeq8.3\times10^{-6}$ V/photon. In this manner one obtains a measured value for the physical cross section for spontaneous de-excitation of $\sigma_s=3.4\times10^{-23}$ cm^2, with an overall experimental uncertainty of a factor of 7.

The measured cross section for spontaneous deexcitation can be related to the laser-induced cross section σ_c for dipole-quadrupole collision [Eq. (4)] using the relation [11,16]

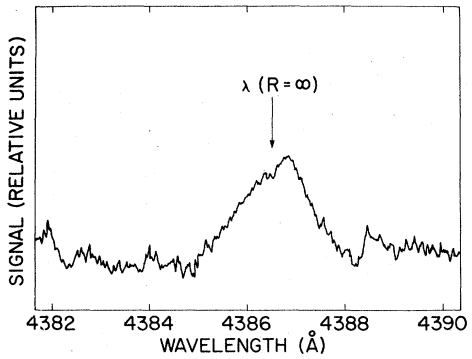

FIG. 4. Magnitude of the spontaneous dipole-quadrupole radiative emission at 4386.5 Å with 50 Torr of Ar buffer gas. The plot has not been corrected for the 0.2-Å spectrometer resolution.

$$\sigma_c=\frac{\pi^2c^2}{\hbar\omega^3\delta\omega}\left(\frac{g[\mathrm{Ba}^*]}{g[\mathrm{Ba}]}\right)^2\left(\frac{P}{A}\right)^{-1}\sigma_s\,, \tag{6}$$

where $\delta\omega$ is the measured FWHM and the $g[\mathrm{Ba}]$, $g[\mathrm{Ba}^*]$ are the ground- and excited-state degeneracies, respectively. Using $\sigma_s=3.4\times10^{-23}$ cm^2 and $\delta\omega=1.5\times10^{12}$ rad/sec, one finds $\sigma_c=6.0\times10^{-25}$ $(P/A)^{-1}$cm^2, where the applied laser power density is in units of W/cm^2. The measured value of σ_c is a factor of 3.3 larger than the value calculated previously using Eq. (4); and considering the uncertainties inherent in such a comparison, the agreement is excellent.

IV. DISCUSSION

The results reported here provide for the first time a direct comparison of stimulated absorption and spontaneous-emission line shapes for the dipole-quadrupole laser-induced collision. In addition, optogalvanic detection is shown to be a sensitive and convenient detection tool for the study of the dipole-quadrupole collision. The ready detection of small changes in steady-state discharge populations that result from laser-induced interactions may also permit the detailed study of multiphoton, [17] collision-induced Raman, and laser-induced charge-transfer processes. [19]

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