Observation of atomic-pair absorption with an incoherent source

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We report the observation of atomic-pair absorption in barium and in barium–thallium vapors using a white-light source. At atomic densities on the order of 10^{17} atoms/cm^3 we measure absorptions of 2.9% cm^{-1} for Ba–Ba and 2.3% cm^{-1} for Ba–Tl. In both cases, the absorption maxima occur at the predicted ($R = \infty$) wavelength and have a full width at half maximum of approximately 15 cm^{-1}.

The term pair absorption or pair excitation[1] refers to a process by which two atoms or molecules collide and absorb a single photon at a frequency corresponding to the sum energy of the two species. The process may be viewed as a virtual excitation followed by collision or, instead, as an absorption by a quasi-molecule formed during collision.[2] Pair excitation in molecular species at high pressure (10 to 100 atm) has been observed in the infrared, where it has been termed a collision-induced simultaneous transition.[3,4]

In this Letter we describe the observation of pair absorption in atomic systems at modest densities ($\sim 10^{17}$ atoms/cm^3). Absorptions of several per cent per centimeter for Ba–Ba and Ba–Tl are reported and are easily seen via a simple white-light absorption measurement. As we describe below, the results of these measurements bear on the study of laser-induced collision cross sections and may provide a convenient means by which to study the interaction potentials of colliding atoms.

We study the processes

$$\mathrm{Ba}(6s^2\,{}^1S_0) + \mathrm{Ba}(6s^2\,{}^1S_0) + \hbar\omega(3394\text{ Å}) \rightarrow \mathrm{Ba}(6p\,{}^1P_1^\circ) + \mathrm{Ba}(5d\,{}^1D_2) \quad (1)$$

and

$$\mathrm{Ba}(6s^2\,{}^1S_0) + \mathrm{Tl}(6p\,{}^2P_{1/2}^\circ) + \hbar\omega(3867\text{ Å}) \rightarrow \mathrm{Ba}(6p\,{}^1P_1^\circ) + \mathrm{Tl}(6p\,{}^2P_{3/2}^\circ). \quad (2)$$

The first of these is observed in pure Ba vapor and is the absorption analog of the Ba–Ba radiative collisional fluorescence that was recently reported by the authors.[5] The second process is observed in a mixture of Ba and Tl vapor.

For process (1), the absorbed photon has energy equal to the sum of the barium $6p\,{}^1P_1^\circ$ and $5d\,{}^1D_2$ levels (see Fig. 1), whereas, for process (2), the photon has energy equal to the sum of the Ba($6p\,{}^1P_1$) level and the Tl($6p\,{}^2P_{3/2}^\circ$) level (see Fig. 2). In both cases the peak absorption occurs at the sum frequency of the levels of the infinitely separated atoms. We term this the $R = \infty$ frequency. These absorption frequencies do not correspond to any (tabulated) characteristic frequencies of the isolated atoms.

The absorption coefficient, $\alpha(\omega)$, for pair absorption is given by the expression:

$$\alpha(\omega) = \frac{\sigma_c(P/A,\omega)\overline{V}\hbar\omega}{(P/A)} \times \left(N_A N_B - \frac{g_A g_B}{g_{A^*} g_{B^*}} N_{A^*} N_{B^*}\right), \quad (3)$$

where N_A, N_B and N_{A^*}, N_{B^*} are the appropriate ground- and excited-state number densities, g_A, g_B, etc., are the corresponding degeneracies, ω is the frequency of the pair absorption, $\overline{V}$ is the mean velocity of collision, and $\sigma_c(P/A,\,\omega)$ is the photon-induced collision cross section for absorption.[2] We note that at low incident flux $\sigma_c(P/A,\,\omega)$ is proportional to P/A, yielding an overall expression for $\alpha(\omega)$ that is independent of power density. For the Ba–Ba process, Eq. (3) yields $\alpha(3394\text{ Å}) = 6.8 \times 10^{-37}\, N_{\mathrm{Ba}} N_{\mathrm{Ba}}$ (atoms/cm^3)^2 cm^{-1}, based on a calculated value $\sigma_c = 2.5 \times 10^{-23}\,(P/A)$ cm^2, where (P/A) is in units of W/cm^2. For Ba–Tl, using $\sigma_c = 2.2 \times 10^{-22}\,(P/A)$ cm^2, we obtain $\alpha(3867\text{ Å}) = 7.1 \times 10^{-36}\, N_{\mathrm{Ba}} N_{\mathrm{Tl}}$ (atoms/cm^3)^2 cm^{-1}.

The experimental setup used to observe pair ab-

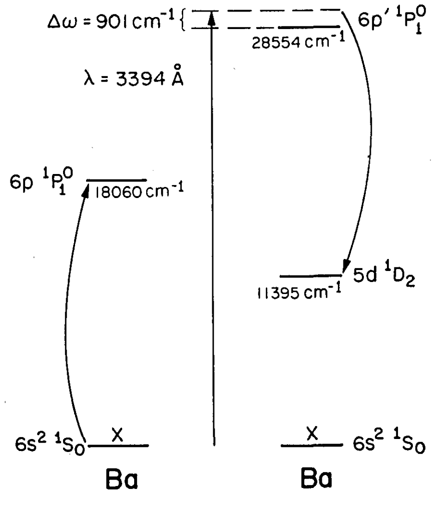

Fig. 1. Pertinent Ba levels for the observation of pair absorption. During the collision of two Ba atoms, a photon is absorbed at 3394 Å, resulting in the simultaneous excitation of one Ba atom to the $6p\,{}^1P_1^\circ$ level and the other Ba atom to the $5d\,{}^1D_2$ level.

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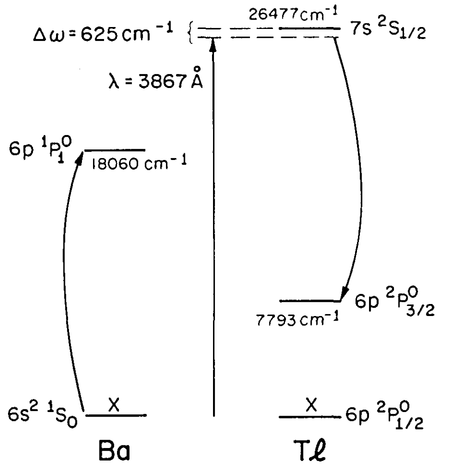

Fig. 2. Pertinent Ba and Tl levels for the observation of pair absorption. During the collision of a Ba atom with a Tl atom, a photon is absorbed at 3867 Å, resulting in the simultaneous excitation of the Ba atom to the $6p\ ^1P_1^\circ$ level and the Tl atom to the $6p\ ^2P_{3/2}^\circ$ level.

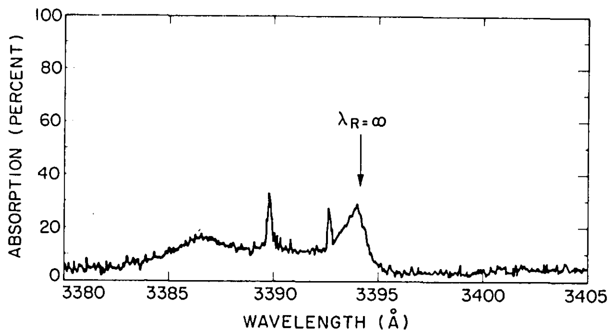

Fig. 3. Observed Ba–Ba pair absorption at 3394 Å. The two narrow absorptions at 3393 and 3390 Å correspond to tabulated Ca transitions, which appear at high cell temperatures. The broad absorption at 3386 Å is unexplained.

sorption consisted of a metal vapor oven capable of operation at temperatures of 1600°C with a hot-zone length of 10 cm. The cell was filled with 500 Torr of argon buffer gas to prevent the metal vapors from condensing on the cold cell windows. A high-pressure Hg–Xe arc lamp was used as the white-light source; the lamp radiation was collimated, passed through the metal vapor cell, and focused onto the slits of a 1-m scanning spectrometer. The system had a resolution of ~0.3 Å, and absorptions as small as 0.5% cm^{-1} were readily detectable. The ground-state number densities were determined from the absorption width of the appropriate atomic resonance line, using the curve of growth method.[6] For the Ba–Ba experiment, the absorption scans were taken at a measured density of $N_{Ba} = 1.8 \times 10^{17}$ atoms/cm^3, whereas, for the Ba–Tl experiment, the densities were measured to be $N_{Ba} = 7.9 \times 10^{16}$ atoms/cm^3 and $N_{Tl} = 1.4 \times 10^{17}$ atoms/cm^3. These densities are approximately 4 orders of magnitude lower than those required for observation of similar effects in molecular systems.[3,4]

The experimentally measured absorption profile for process (1) in Ba–Ba is shown in Fig. 3. The absorption maximum occurs at the predicted ($R = \infty$) wavelength of 3394 Å and has a full width at half maximum of 15 cm^{-1} (all wavelengths given in air). This agrees closely with the observed width of 20 cm^{-1} for the emission process reported in Ref. 5. The two sharp lines superimposed on the pair absorption are due to calcium impurities that are present when the cell is operated at high temperatures.[7] The peak absorption of approximately 29% agrees well with the calculated absorption of 22% as obtained from Eq. (3). From the measured absorption we infer an experimentally determined $\sigma_c = 3.3 \times 10^{-23}\ (P/A)$ cm^2, which is in good agreement with both the theoretical value of $\sigma_c = 2.5 \times 10^{-23}\ (P/A)$ cm^2 and the measured value of $\sigma_c = 5.1 \times 10^{-23}\ (P/A)$ cm^2, as obtained from the corresponding emission process.[5]

The absorption scan for process (2) in Ba–Tl is shown in Fig. 4. The absorption maximum again occurs at the ($R = \infty$) wavelength of 3867 Å, and the measured absorption of approximately 23% agrees reasonably well with the predicted value of 78%. From these data we infer that $\sigma_c = 6.5 \times 10^{-23}\ (P/A)$ cm^2, as compared with the calculated value of $\sigma_c = 2.2 \times 10^{-22}\ (P/A)$ cm^2. No absorption at 3867 Å was observed when either Ba or Tl was present in the cell alone.

One application of the pair-absorption process may be to the study of the interaction potentials of colliding atoms. For the Ba–Ba case, an approximate calculation indicates that the resonant dipole–dipole interaction C_3/R^3, with $C_3 = 1.3 \times 10^{-35}$ erg-cm^3, is the dominant term in the interaction energy. This interaction results in a symmetric, orientationally dependent splitting of the interatomic potentials, which in turn implies an approximately symmetric lineshape for the absorption profile. If additional C_6/R^6 terms are included in the interaction potentials, an asymmetric tail is predicted. For the Ba–Tl case, the nonresonant dipole–dipole interaction is dominant. Using the sign convention of Ref. 2, we calculate a relative $C_6 = -4.9 \times 10^{-57}$ erg-cm^6, which implies a red asymmetry for the absorption profile. This is in agreement with the long-wavelength tail present in the absorption scan of Fig. 4.

This work represents a simple and accurate technique for measuring photon-induced collision cross sections. In addition, the types of measurement reported here may be of particular value when used in conjunction with the inversion process recently proposed by Falcone.[8] Here, intense laser radiation applied at the

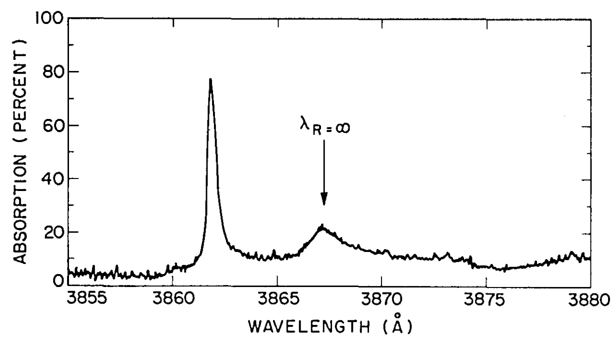

Fig. 4. Observed Ba–Tl pair absorption at 3867 Å. The narrow absorption at 3862 Å corresponds to a tabulated Ba transition.

frequency of the pair absorption, i.e., the sum of the frequency of an allowed and nonallowed transition of two species, can result in an inversion to ground of the less dense of these species. Since practical sum frequencies often lie in the region of the rare-gas–halide lasers, the process may be useful for inverting the resonance line of species and also for inverting nonallowed transitions to accomplish energy storage. Finally, we note that pair absorption may be observable in the spectra of natural systems, such as planetary and stellar atmospheres.

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