Measurement of Transition Dipole Moments in Lithium Dimers
Using Electromagnetically Induced Transparency

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We have observed electromagnetically induced transparency in a Doppler broadened molecular cascade system using fluorescence detection. We demonstrate that the power-dependent splitting of lines in the upper-level fluorescence excitation spectrum can be used as a new spectroscopic tool for the measurement of molecular transition dipole moment functions.

Coherence phenomena in laser-atom interactions have been a focus of interest for decades, beginning with Fano’s pioneering studies [1]. Coherent population trapping [2], electromagnetically induced transparency (EIT) [3], lasing without inversion [4], and ultrashort propagation of light [5], among others, have been predicted and observed in atomic systems.

Fewer experimental studies have addressed coherence phenomena in molecular systems [6] and, in particular, the possible occurrence of EIT [7]. This is perhaps due to the small size of typical molecular transition dipole moments. In addition, unlike atoms, even the simplest molecules are open systems in that every excited molecular rovibrational level is radiatively coupled to many more energy levels than any atomic excited state. Therefore, coherence effects in molecular systems are more challenging in terms of both experimental observation and development of theoretical analyses.

In a previous paper [8] we emphasized that the Autler-Townes (AT) splitting can be used in a four-level system as a way to facilitate all-optical control of molecular angular momentum alignment. We also demonstrated that molecular transition dipole moments can be measured through AT splitting, as done, for example, by Quesada et al. in pulsed laser experiments on the H₂ molecule [9]. Thus, coherence effects may allow measurement of important molecular parameters. In this Letter we show that EIT can be observed even without sub-Doppler resolution using two frequency stabilized tunable lasers in a three-level system. We also demonstrate the use of this coherent effect to measure the transition dipole moment matrix element between two of the excited molecular levels using a much less demanding experimental arrangement than in [8].

A characteristic signature of EIT for the system shown in Fig. 1 is the enhanced transmission of a weak probe nearly resonant with the $|1\rangle \rightarrow |2\rangle$ transition, in the presence of a strong coupling field resonant with the $|2\rangle \rightarrow |3\rangle$ transition. EIT, however, can also be recognized by the appearance of a sharp dip in the fluorescence excitation spectrum of the intermediate level [10], under resonance conditions for the probe. The connection between this feature and EIT can be best understood if we consider that a cascade system becomes formally equivalent to a lambda system after moving its topmost state to a position below the middle level [3(c)]. It is well known that, under EIT conditions, the population of the highest energy level of a lambda system displays a dip, which signals the emergence of a dark state. The same holds true for the population of the middle level of a cascade system. The fluorescence from the highest level (3) is also affected by the coupling field, especially if this field is sufficiently strong. The upper-level excitation spectrum, obtained by scanning the probe laser while holding the coupling laser on resonance and monitoring (filtered) side fluorescence from the

![Diagram](image)

FIG. 1. \(^7\)Li₂ three-level cascade scheme: The weak probe laser, L₁ (15642.636 cm⁻¹), was used to excite molecules from the ground state level \(X^1\Sigma^+_g(v_1 = 4, J_1 = 15)\) to an excited intermediate level \(A^1\Sigma^+_u(v_2 = 13, J_2 = 14)\). The laser, L₂ (17053.954 cm⁻¹), resonantly coupled the intermediate level to a higher electronic state level \(G^1\Pi_g(v_3 = 11, J_3 = 14, f)\).
upper level, shows a symmetrically split line shape, which is substantially narrower than the full Doppler width of the transition, and displays a separation between the split components that varies linearly with the Rabi frequency of the coupling laser (Aulter-Townes splitting). In contrast, the sharp hole in the excitation spectrum from the intermediate level is largely independent of the strength of the coupling field.

We use the power-dependent splitting of the level-3 excitation spectrum to measure directly the transition dipole moment matrix element between levels 2 and 3. Traditionally, transition dipole moments are measured from resolved fluorescence spectral intensities and lifetimes [11]. Such methods are time consuming and suffer from potential systematic errors. Among these, the wavelength and polarization dependence of the light detection system’s quantum efficiencies is the predominant source of error. Relative transition moments can also be calculated using ab initio methods. The experimental method described here permits determination of the absolute value of the transition dipole moment matrix element, which, in turn, requires an accurate measurement of the coupling field Rabi frequency, i.e., the coupling field spot size and power.

The experimental setup was similar to that of Ref. [8] in terms of the molecular sample conditions, optical detection, and laser systems, except that it requires only two, instead of three, lasers (as shown in Fig. 1). The weak probe laser, L1, excited molecules from the ground state level, \(X^1\Sigma_g^+(v_1 = 4, J_1 = 15)\), to an intermediate level, \(A^1\Sigma_g^+(v_2 = 13, J_2 = 14)\). The laser, L2, resonantly coupled the intermediate level to a higher electronic state level, \(G^1\Pi_g(v_3 = 11, J_3 = 14, f)\). The two laser beams were counterpropagating coaxially, and linearly polarized in a common direction. By using a monochromator as a narrow-band filter, the population of \(A^1\Sigma_g^+(v_2 = 13, J_2 = 14)\) was monitored by detecting the fluorescence from this level to the ground rovibrational level, \(X^1\Sigma_g^+(v_1 = 4, J_1 = 13)\). Similarly, the population of \(G^1\Pi_g(v_3 = 11, J_3 = 14, f)\) was monitored by detecting fluorescence at auxiliary levels \(A^1\Sigma_g^+(v_2 = 12, J_2 = 14)\). Excitation spectra were obtained by scanning the probe laser frequency, which was calibrated to \(\pm 0.002\) cm\(^{-1}\) using iodine calibration [12].

When L1 was scanned in the absence of L2, while simultaneously monitoring the \(A^1\Sigma_g^+(v_2 = 13, J_2 = 14)\) fluorescence, the usual Doppler broadened excitation spectrum was observed. When the power of the coupling laser was increased, a sharp dip emerged (as shown in Fig. 2). This dip is a signature of EIT [10].

![FIG. 2. Measured excitation spectra from level 2 along with the corresponding simulations using Eqs. (1a) and (4). Dephasing parameters are \(\gamma_{12}/2\pi = 6.78\) MHz, \(\gamma_{13}/2\pi = 0.85\) MHz, \(\gamma_{23}/2\pi = 1.69\) MHz. The coupling field power is 470 mW.](image)

We next monitored the upper-level fluorescence as described above. When L2 was below saturation (<10 mW), scanning the probe laser produced the narrow spectrum shown in Fig. 3(a). The effect of increasing the coupling field power to 470 mW is shown in Fig. 3(b). The line shape is significantly power broadened and symmetrically split into two non-Lorentzian lines. Figure 4 shows the splitting as a function of the coupling field amplitude. When the Rabi frequency of the coupling laser was made larger than the partially Doppler broadened line, the splitting became observable and it was found to be proportional to the Rabi frequency.

In order to confirm the nature of the fluorescence line shapes in the presence of EIT, we solved the density matrix equations for the open, three-level, cascade system of Fig. 1. The probe laser (L1) was treated perturbatively and the coupling field (L2) was treated exactly. As described in Ref. [8], the linearly polarized electric fields can be approximated by

\[ E_i(\hat{r}, t) = E_i\hat{\varepsilon}\exp[-(r/w_i)^2]\cos(k_i z - \omega_i t), \]

where \(w_i, k_i, \) and \(\omega_i\) denote the spot size at the beam waist, the wave number, and the frequency of the ith laser, respectively, and \(\hat{\varepsilon}\) is the unit polarization vector. In steady state, the populations of the second and third levels for a molecule with orientation \(M\), radial position \(r\) relative to the common axis of the laser beams, and velocity \(v_z\) are given by

\[ \rho_{22}(r, v_z, t \to \infty) = \frac{-\Omega_{2M}^2}{2F_M(\Delta_2)} \text{Im} \left[ \frac{(\Delta_1 + \Delta_2 + i\gamma_{13})[\Delta_2^2 + \gamma_{23}^2 + \Omega_{2M}\gamma_{23}]}{\Delta_1 + \Delta_2 + i\gamma_{13}} - \frac{\Omega_{2M}^2}{4}(1 - \frac{W_2}{W_1})(\Delta_2 - i\gamma_{23}) \right] \] (1a)

\[ \rho_{33}(r, v_z, t \to \infty) = \frac{\Omega_{1M}^2\Omega_{2M}^2}{8W_1F_M(\Delta_2)} \text{Im} \left[ -2\gamma_{23}(\Delta_1 + \Delta_2 + i\gamma_{13}) + W_2(\Delta_2 - i\gamma_{23}) \right] \text{Im} \left[ (\Delta_1 + \Delta_2 + i\gamma_{13})(\Delta_1 + i\gamma_{12}) - \Omega_{2M}^2/4 \right]. \] (1b)
where $m$ the two lasers (frequencies, the probe and coupling lasers from the molecular transition In Eqs. (1a) and (1b), the velocity-dependent detunings of $V_{i}$, $M$, depend on both the orientation $1, 2$, and the averaging over the Doppler and transverse laser transitions induced by $L_{1}$ and $L_{2}$ respectively, we have [13]

$$\mu_{12}^{M} = \mu_{||}|\langle v_{1}|v_{2}\rangle|\sqrt{(J_{1}^{2} - M^{2})/(2J_{1} + 1)(2J_{1} - 1)},$$

(3a)

$$\mu_{23}^{M} = \mu_{\perp}|\langle v_{2}|v_{3}\rangle|\sqrt{J_{2}(J_{2} + 1)},$$

(3b)

where $v_{i}$ is the vibrational quantum number for level $i$, and $\mu_{||}$ ($\mu_{\perp}$) is the $|1\rangle \rightarrow |2\rangle$ ($|2\rangle \rightarrow |3\rangle$) electronic transition dipole moment, which is along (perpendicular to) the internuclear axis.

In Eq. (1), $W_{i}$ is the damping rate of the $i$th level, including both radiative and collisional contributions. The decay rate of the coherence between levels $i$ and $j$ ($i \neq j$) is $\gamma_{ij} = (W_{i} + W_{j})/2 + \gamma_{ij}^{p}$, where $\gamma_{ij}^{p}$ is the pure dephasing contribution induced by phase-changing collisions. For open systems, $W_{32} < W_{3}$, where $W_{32}$ is the level-3 → level-2 decay rate. In a closed system, $W_{32} = W_{3}$, and Eqs. (1a) and (1b) simplify considerably. The signal is obtained from Eqs. (1) by summing over $M$ and averaging over the Doppler and transverse laser profiles. The final excitation spectrum $S_{i}(\Delta_{1})$ from level $i$ ($i = 2, 3$) is

$$S_{i}(\Delta_{1}) = \sum M \int_{0}^{\infty} r dr \int_{-\infty}^{\infty} dv_{z} N(v_{z}) \rho^{M}_{ii}(r, v_{z}, t \rightarrow \infty),$$

(4)

where $N(v_{z})$ is the Maxwell velocity distribution.

The parameters in Eqs. (1a) and (1b) are determined as follows: From Ref. [14], the lifetime of the intermediate level 2 is known, $W_{2}^{-1} = 18$ ns. Although $W_{3}^{-1}$ and the $\gamma_{ij}$ have not been directly measured, a set of values which reproduce the experimental line shapes in Figs. 2 and 3 can be found. In the following we take $W_{3}^{-1} = 0.5W_{2}^{-1}$.
consistent with Ref. [8], and the three collisional dephasing rates reported in Fig. 2. However, as is shown below, the upper-level splitting does not critically depend on these parameters. The branching ratio was set to $W_{32}/W_3 = 0.1$, indicating an open system, although all calculated line shapes in Figs. 2 and 3 remain essentially unchanged for $W_{32}/W_3 < 0.5$. For the spatial and Doppler averaging in Eq. (4), we used the measured value of the FWHM Doppler linewidth 2.6 GHz, and the beam spot size parameters $w_1 = 208 \ \mu m$ and $w_2 = 557 \ \mu m$ for $L_1$ and $L_2$, respectively.

Figures 2 and 3 also show the line shape simulations using Eqs. (1) and (4). In order to obtain agreement with the experimental spectra in Fig. 3(b), the Rabi frequency of the second laser, $\Omega_{2,M}$, was varied until the peak-to-peak separation in $S_3(\Delta t)$ matched the experimental value. The simulated splitting was found to be approximately $0.42 \mu m / \Omega_{2,M}$ for sufficiently large $E_2$, allowing $\mu_{\perp}$ to be determined experimentally from $S_3(\Delta t)$, once $|\langle \nu_2 | \nu_3 \rangle|$ and $E_2$ are known.

The linear dependence of the upper-level splitting on $E_2$ is confirmed experimentally in Fig. 4, which also shows simulations using several sets of collisional dephasing parameters. Collisional dephasing influences only the low power region in which the emergence of the dip depends on details of the linewidth. Once the splitting is sufficiently large, it becomes independent of homogeneous broadening and scales linearly with $E_2$. The best match between our theory and experiment is obtained for an electronic transition dipole moment $\mu_{\perp} = 2.4 \pm 0.2$ a.u. for the $G^1\Pi_g - A^1\Sigma^+$ system [15]. The main sources of uncertainty are slight variations in the laser power and frequency of $L_2$, which are indicated by the error bars in Fig. 4 obtained by combining independent measurements. Recent ab initio calculations of these transition dipole moment matrix elements, 2.44 a.u. [16] and 2.28 a.u. [17], are in excellent agreement with our measured value.

An experimental method to determine systematically the transition dipole moment matrix elements for a sequence of electronic states is of critical value. For example, in the Rydberg series $n\Lambda_g(v) \rightarrow A^1\Sigma^+_g$, $n\Lambda_g(u) = n s^1\Sigma^+_g$, $n d^1\Sigma^+_g$, and $n d^1\Pi_g$, transition moments to members of the same Rydberg series are expected to follow a simple scaling rule,

$$M_{n\Lambda}(R) \equiv \langle n\Lambda | e^{|A^1\Sigma^+} n^{-3/2} M_{1\lambda}(R).$$

Since, at $n > 10$, successive $n$ members of the same $\lambda, \Lambda, v$ series are separated by less than 220 cm$^{-1}$, it should be possible to measure the transition moment matrix elements for many consecutive members of several Rydberg series. These measurements could have considerable diagnostic value and would provide new insights into the electronic structure and dynamics of Rydberg states.

In summary, we have observed EIT in a Doppler broadened cascade molecular system using fluorescence detection. We have demonstrated that the power-dependent splitting in the level $3 \rightarrow 2$ excitation spectrum can be used as a new spectroscopic diagnostic of transition dipole moment functions in molecular (and atomic) systems.

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[7] Claims to this effect have been advanced in N. N. Rubtsova, Opt. Spectrosc. 91, 53 (2001).
[15] Reference [8] reported a value of 3.4 a.u. However, after omitting an erroneous factor of $1/\sqrt{2}$ in Eq. (3) of Ref. [8] [J. Qi et al., Phys. Rev. Lett. erratum (to be published)], the value becomes 2.4 a.u., in excellent agreement with the present measurement.
[16] S. Magnier (private communication).