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Rapid Communications

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Observation of Autler-Townes splitting in the multiphoton ionization of H_2: Measurement of vibronic transition moments between excited electronic states

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We report the first observation of Autler-Townes splitting in multiphoton ionization of molecules and its application to measure vibronic transition moments between excited electronic states. The effect was observed in the two-color, four-photon ionization of H_2 via the resonant levels $E,F\,{}^1\Sigma_g^+$, $v=6$, $J=1$ and $D\,{}^1\Pi_u$, $v=2$, $J=2$. Calculations give good fits to the observed spectra. They yield a vibronic transition moment of 2.0 ± 0.5 a.u. between the above excited states, in agreement with the *ab initio* value 1.97 a.u. calculated by Huo and Jaffe.

Multiphoton ionization (MPI) of molecules is a subject of great interest for its potential as an analytic tool in excited-state spectroscopy, molecular-dynamics studies (such as ionization, dissociation, and reaction), and species identification. The strong interaction between molecules and high-powered laser radiation in multiphoton experiments may produce nonlinear effects. Two such effects, power-broadening and optical Stark *shift* of molecular spectral lines, have been observed in some recent multiphoton experiments.[1-10] The understanding of these effects is important if multiphoton processes are to become a practical and common technique in analytic chemistry.

In this Rapid Communication, we report the observation of another nonlinear effect, the Autler-Townes splitting[11] of molecular spectral lines. Although it has been observed in atoms[12] and in rovibrational lines in ground electronic states in molecules,[11,13,14] this appears to be the first report of its observation in electronic-excited states of molecules. The calculated MPI spectra based on a density-matrix theory give good fits to the observed spectra. These fits yield a value of the vibronic transition moment in agreement with the calculated value of Huo and Jaffe.[15] We compare the use of the Autler-Townes splitting to measure transition moments between excited electronic states in molecules with other methods[16-20] and discuss its advantages.

The Autler-Townes effect (also known as ac, optical, or dynamical Stark splitting) is the high-frequency analog of the splitting of two degenerate molecular levels by a dc Stark field. If two molecular levels connected by an electric dipole transition moment d interact with a "pump" laser beam of electric-field amplitude E and a frequency detuning Δ, the separation S for the two new eigenenergies of the "molecule+field" system is given by

$$S=(\Delta^2+\chi^2)^{1/2}\ , \tag{1}$$

upon the solution of a simple 2×2 eigenvalue problem. Here $\chi\equiv dE/\hbar$ is the Rabi frequency and we assume that *χ is much larger than the molecular relaxation rates and the laser bandwidth.* In double-resonance experiments, a second laser is used to probe these two split eigenlevels by inducing transitions to a third level, revealing two distinct resonance peaks. One sees from Eq. (1) that when $\chi^2\gg\Delta^2$, the Autler-Townes separation $S\approx\chi$ is proportional to E, unlike the optical Stark shift which is proportional to E^2. From Eq. (1), one sees that if Δ and E are known, a measurement of S will give the transition moment d. It was proposed using this method to measure molecular transition moments with MPI in H_2 as an example.[21]

The present experiment was carried out in H_2 with the MPI energy scheme shown in Fig. 1. Two pulsed neodymium-doped yttrium aluminum garnet (Nd:YAG)-pumped dye lasers (10-Hz repetition rate) were set to arrive coincident in time in the ionization region of a time-of-flight mass spectrometer (see Fig. 1 in Ref. 22 for a similar experimental setup). One laser operated on rhodamine 590 dye pumped by the second harmonic of the Nd:YAG laser. Tunable light (568–572 nm) from this laser was frequency doubled and focused into a high-pressure H_2 Raman shifter. The fourth anti-Stokes beam (at wavelength 193 nm, bandwidth ≈ 0.7 cm^{-1}, pulse length ≈ 5 ns, and 80 μJ/pulse, ≈ 8 mm diam) was isolated by matched Pellin-Broca prisms, which compensated for beam walkoff due to wavelength scanning, and focused into the chamber by a 125-mm lens to an estimated 10-μm beam waist. This uv beam was tuned near the $X(v=0,J=1)$-$E,F(v=6,J=1)$ two-photon transition.

The sample region of the vacuum chamber contained H_2 gas (supplied by Matheson) at 2.3 mTorr. A repeller-extractor combination (typically biased at ≈ 200 V/cm) accelerated the laser-ionized H^+ and $H_2{}^+$ ions through the extractor slit, which also served as a vacuum wall for differential pumping, and into the time-of-flight chamber ($\approx 10^{-7}$ Torr). Mass-selected $H_2{}^+$ ions were measured by a boxcar averager as the uv beam was scanned. A typical MPI spectrum is shown in Fig. 2(a).

The second laser is a Nd:YAG-pumped dye laser (0.2-cm^{-1} bandwidth and 10-ns pulse length) operating on LDS750 laser dye at set wavelengths around 726 nm. After collimation to 4.0 ± 0.4 mm diam, the beam was overlapped with the uv beam inside the ionization region of the sample chamber. This infrared (ir) laser was attenuated by insertion of up to three filters (Corning 7-54) in the beam path, each with a measured transmission of 0.44 at 726 nm. The unattenuated pulse energy was 10 mJ, measured by a calibrated calorimeter. Overlap of the unfocused ir laser with uv laser focal point was optimized after insertion of each filter by setting the uv laser on the satellite peak of the Autler-Townes doublet and adjusting the ir laser positioning for maximum signal. This method compensated for imperfectly aligned filters and was found to give reproducible MPI spectra (within < 10%) over the few weeks that the data were taken. Figures 2(b)–2(d) show one set of such MPI spectra at a fixed ir laser detuning $\Delta_b = 4.8$ cm^{-1} from the $E,F(v=6,J=1)$-$D(v=2,J=2)$ resonance but at different pulse energies. The increases in the peak separation and the satellite peak height at higher ir laser power are the characteristics of

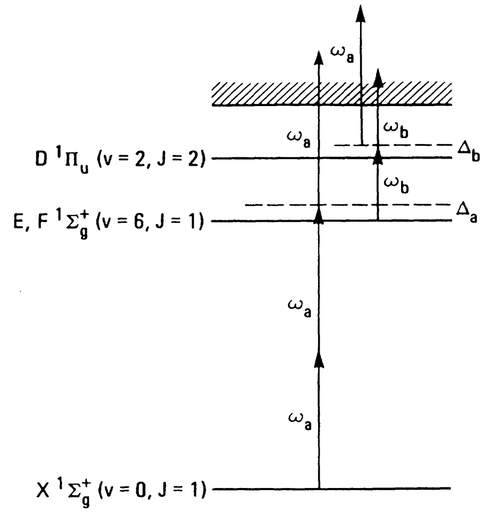

FIG. 1. Schematic H_2 energy-level diagram showing the multiphoton ionization with a uv (ω_a) and an ir (ω_b) lasers.

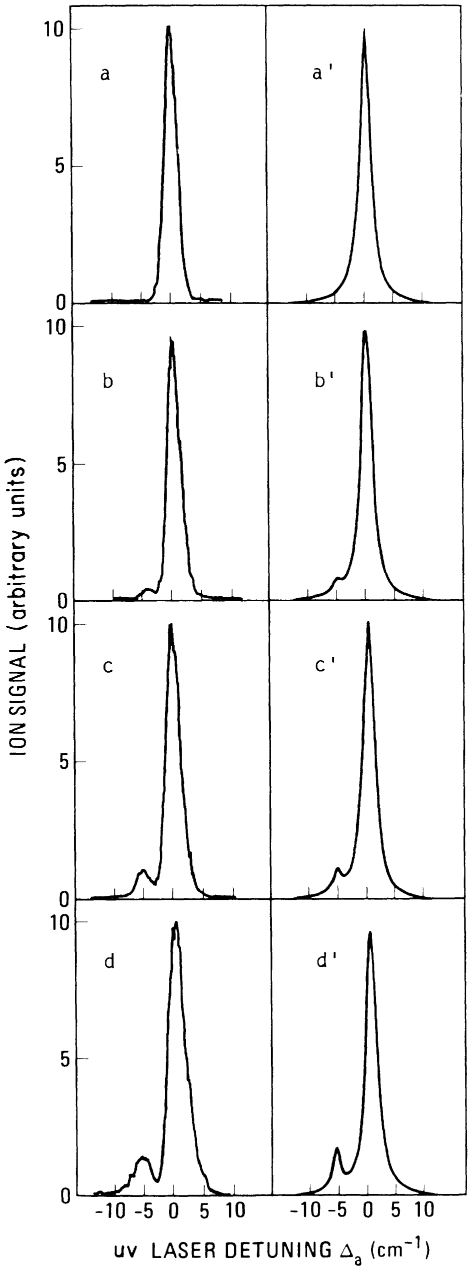

FIG. 2. Comparison of the calculated multiphoton $H_2{}^+$-ion spectra [(a)′-(d)′] with the corresponding observed spectra [(a)-(d)] at ir laser pulse energies: (a) 0 mJ; (b) 1.9 mJ; (c) 4.4 mJ, and (d) 10 mJ. The ir laser detuning Δ_b is 4.8 cm^{-1}.

the Autler-Townes effect. The same effect was observed for several detunings of difference magnitudes and/or of opposite sign.

Labeling the $X(v=0,J=1)$, $E,F(v=6,J=1)$, and $D(v=2,J=2)$ levels as 1, 2, and 3 (with energies $\hbar\omega_i$), respectively, and the uv and the ir lasers as lasers a and b (with frequencies ω_x), respectively, we model the MPI process as a two-color double optical resonance as shown in Fig. 1. The density-matrix equations of motion for the system are given by[21]

$$d\sigma_{11}/dt=\gamma_{21}\sigma_{22}+\gamma_{31}\sigma_{33}+\mathrm{Im}(\chi_{12}\sigma_{12}) \ , \tag{2}$$

$$d\sigma_{22}/dt=-\Gamma_2\sigma_{22}+\mathrm{Im}(\chi_{23}^*\sigma_{23})-\mathrm{Im}(\chi_{12}^*\sigma_{12}) \ , \tag{3}$$

$$d\sigma_{33}/dt=-\Gamma_3\sigma_{33}-\mathrm{Im}(\chi_{23}^*\sigma_{23}) \ , \tag{4}$$

$$\begin{aligned} d\sigma_{12}/dt=&-(i\Delta_a+\Gamma'_{21}/2)\sigma_{12}\\ &+i\chi_{12}(\sigma_{22}-\sigma_{11})/2-i\chi_{23}^*\sigma_{13}/2 \ , \end{aligned} \tag{5}$$

$$\begin{aligned} d\sigma_{23}/dt=&-(i\Delta_b+\Gamma'_{32}/2)\sigma_{23}\\ &+i\chi_{23}(\sigma_{33}-\sigma_{22})/2+i\chi_{12}^*\sigma_{13}/2 \ , \end{aligned} \tag{6}$$

$$\begin{aligned} d\sigma_{13}/dt=&-(i\Delta_a+i\Delta_b+\Gamma'_{31}/2)\sigma_{13}\\ &+i\chi_{12}\sigma_{23}/2-i\chi_{23}\sigma_{12}/2 \ , \end{aligned} \tag{7}$$

where $\chi_{12}\equiv\sum_k\chi_{2k}\chi_{1k}/2\Delta_k$ is the effective two-photon Rabi frequency and the χ_{ij} are the Rabi frequencies defined in Eq. (1). The detunings Δ_a, Δ_b, and Δ_k are defined as $\Delta_a=2\omega_a-(\omega_2-\omega_1)$, $\Delta_b=\omega_b-(\omega_3-\omega_2)$, and $\Delta_k=\omega_k-\omega_1-\omega_a$. The γ_{ij} is the decay rate from state i to state j, while Γ_i denotes the total decay rate from state i to all the other states. This may include spontaneous radiative decay, collisional quenching, and laser-induced photoionization. The effective transverse relaxation rates Γ'_{ij} are given in terms of the transverse relaxation rates Γ_{ij} and the laser full width at half maximum bandwidths γ_a and γ_b as $\Gamma'_{21}=\Gamma_{21}+2\gamma_a$, $\Gamma'_{32}=\Gamma_{32}+\gamma_b$, and $\Gamma'_{31}=\Gamma_{31}+2\gamma_a+\gamma_b$. In Eqs. (2)-(7), the laser field fluctuations have been approximated by the well-known phase-diffusion model with the resulting laser line shapes being Lorentzian.

Since both lasers are linearly polarized, the selection rule $\Delta M_J=0$ holds so that there are three ($M_J=0,\pm1$) independent channels of MPI contributing to the total ion signal. The two-photon Rabi frequency χ_{12} is calculated from the two-photon vibronic transition moment in Ref. 15 and the rotational factors from Ref. 23. With the uv laser intensity $I_a\approx10^{10}$ W/cm^2, χ_{12} is only about 10^9 s^{-1} (due to large intermediate-state energy detunings Δ_k). The radiative decay rate of level 2 has been measured[10] to be 10^7 s^{-1}. The radiative decay rate of level 3 is estimated to be 3×10^8 s^{-1} based on *ab initio* calculation[24] and its radiative decay to level 2 alone should, therefore, be much smaller. Collisions are negligible due to very low pressure. The ionization cross section from the level 2 by the uv laser is estimated[25,26] to be 2.6×10^{-18} cm^2 so that the ionization rate is 2.6×10^{10} s^{-1}. The uv ionization cross section from level 3 is estimated from Ref. 26 to be $\leq10^{-18}$ cm^2 for its final energy is much higher above the ionization threshold than that for level 2. We have performed calculations with values of this cross section $\leq10^{-18}$ cm^2 and found that the spectra changed only very little while the peak separation (important in determining the transition moment) remained unchanged due to dominance by other factors such as the Rabi frequency (see discussions below). We came to the same conclusion when we tested the ir ionization cross section from level 3 by letting its value go as high as 10^{-16} cm^2. The relative insignificance of the ir ionization rate is due to the moderate intensity (≤8 MW/cm^2) of the ir radiation. The vibronic transition moment (Ref. 27) μ_{23} is an adjustable parameter in the fitting procedure. The rest of the parameters such as the laser bandwidths are experimentally determined. With the initial conditions that all the population is in the ground level 1, Eqs. (2)-(7) are numerically integrated for the interaction time $T=5$ ns to obtain $\sigma_{ii}(T)$. Since we see from above that the laser-driven rates dominate over the spontaneous decay rates, the ion signal is given to an excellent approximation by the conservation of total number of molecules, $P_{\mathrm{ion}}=1-\sum_i\sigma_{ii}(T)$. The results are then Doppler averaged for 300 K.

In the fitting process, the calculated spectrum *for zero ir intensity* is normalized in height with the corresponding experimental spectrum. This is necessary because the ion signal was not measured on an absolute scale. It does not affect the subsequent determination of μ_{23}. Then the peak separations of an entire set of observed spectra *for nonzero ir powers* can be fitted with one value of μ_{23}. One such set of calculated spectra is shown in Fig. 2 [(a')-(d')] for comparison. This procedure yields a value for μ_{23} to be 2.0 ± 0.5 a.u., where the estimated errors are largely due to the uncertainty in the measured average ir intensity. This is in good agreement with the *ab initio* value 1.97 a.u. calculated by Huo and Jaffe.[15] In the future, the use of narrow-band single-mode lasers will improve the accuracy of the experiment and facilitate the modeling.

We note that in the above method, the determination of the peak separation of the Autler-Townes doublet (and hence χ) is a frequency measurement, which can be done usually with high accuracy. Another advantage of the method is that in the strong saturation regime, the accuracy of the determined transition moment does not depend critically on precise knowledge of the molecular relaxation rates, the photoionization rates, or the laser bandwidths. To illustrate this point, we compare the value of 6.3 cm^{-1} for the peak separation obtained from fitting the results of Eqs. (2)-(7) to Fig. 2(d), with that of S calculated from Eq. (1) in which all relaxation and decay rates are neglected. Using the measured value of the vibronic transition moment, we obtain 3.6 cm^{-1} for $M_J=\pm1$ and 4.1 cm^{-1} for $M_J=0$ (corresponding to frequencies $\approx10^{11}$ s^{-1}) for the values of χ_{23} at 10 mJ ir pulse energy. These are much larger than the molecular relaxation rates, the photoionization rates, and the laser bandwidths, indicating strong saturation. Substitution of the above values of χ_{23} and the ir laser detuning $\Delta_b=4.8$ cm^{-1} into Eq. (1) gives 6.0 cm^{-1} ($M_J=\pm1$) and 6.3 cm^{-1} ($M_J=0$) for the peak separation S. These values are indeed almost identical to the fitted value 6.3 cm^{-1}.

One may extend the above measurement to obtain the vibronic transition moments of vibrational bands within the same pair of electronic states and attempt to deduce the *electronic* transition moment by the R-centroid approximation. Field and co-workers[16,17] have viewed the conventional methods (absorption coefficients, fluorescence intensities, and radiative lifetimes)[18-20] of determining the transition moment and discussed their drawbacks compared to their laser gain method. In order to obtain absolute values of the transition moments, these techniques generally require absolute measurements of populations, fluorescence intensities, or lifetimes of radiative decay to numerous lower states, whereas the method here is pairwise state selective, independent of absolute population and requires only the measurement of laser intensity and frequency detuning. These features makes it particularly advantageous for measuring transition moments between excited electronic states.

In summary, we have observed Autler-Townes splitting in excited electronic states of molecules using MPI of H_2. Calculated results give good fits to the observed spectra. We have determined the $E,F(v=6)$-$D(v=2)$ vibronic transition moment to be 2.0 ± 0.5 a.u., in agreement with the *ab initio* value 1.97 a.u. of Huo and Jaffe.[15] The method appears well suited for extracting transition moments between stable excited states. It is possible, in principle, to extend the measurement to deduce electronic transition moments by the R-centroid approximation.

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