Observation of Doppler-Free Two-Photon Absorption in the ν_3 Bands of CH_3F†

William K. Bischel and Patrick J. Kelly*
Department of Applied Science, University of California, Davis-Livermore, California 94550

and

Charles K. Rhodes
Lawrence Livermore Laboratory, University of California, Livermore, California 94550
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We report the first observation of Doppler-free two-photon absorption in a molecule using two fixed-frequency infrared optical fields in combination with molecular Stark tuning. The coincidences of the $P14$ and $P30$ lines of two oppositely directed cw CO_2 lasers at 9.4 μm with the $R(1,1)_0 \rightarrow \nu_3$ and $R(2,1)_{\nu_3} \rightarrow 2\nu_3$ lines of $^{12}CH_3F$ are used to measure the pressure-broadening coefficient ($\Delta\nu_p = 41.3 \pm 1.0$ MHz/Torr) and pressure shift ($\Delta\nu_s = 2.1 \pm 0.1$ MHz/Torr) of the $0 \rightarrow 2\nu_3$ transition.

Doppler broadening reduction in two-photon absorption via oppositely directed photons has been previously demonstrated in atomic vapors using one or more visible lasers.[1] We report the first experimental observation using this technique in a molecule (CH_3F) using fixed-frequency infrared (CO_2, 9.4 μm) radiation. From laser Stark spectroscopy data[2] it is found that there are several near coincidences of the P-branch lines of the 9.4-μm band of the CO_2 laser with the ν_3 (C-F stretching vibration) bands of $^{12}CH_3F$. In particular as shown in Fig. 1(b), we select the coincidences of the $P14$ line with the $R(1,1)$ transition of the $0 \rightarrow \nu_3$ fundamental band and the $P30$ line with the $R(2,1)$ transition of the $\nu_3 \rightarrow 2\nu_3$ hot band. The frequency difference between the sum of the two laser lines and the selected two-photon transition is ~139 MHz. This transition can easily be tuned into resonance by applying a dc Stark field. Since $^{12}CH_3F$ is a symmetric-top molecule,

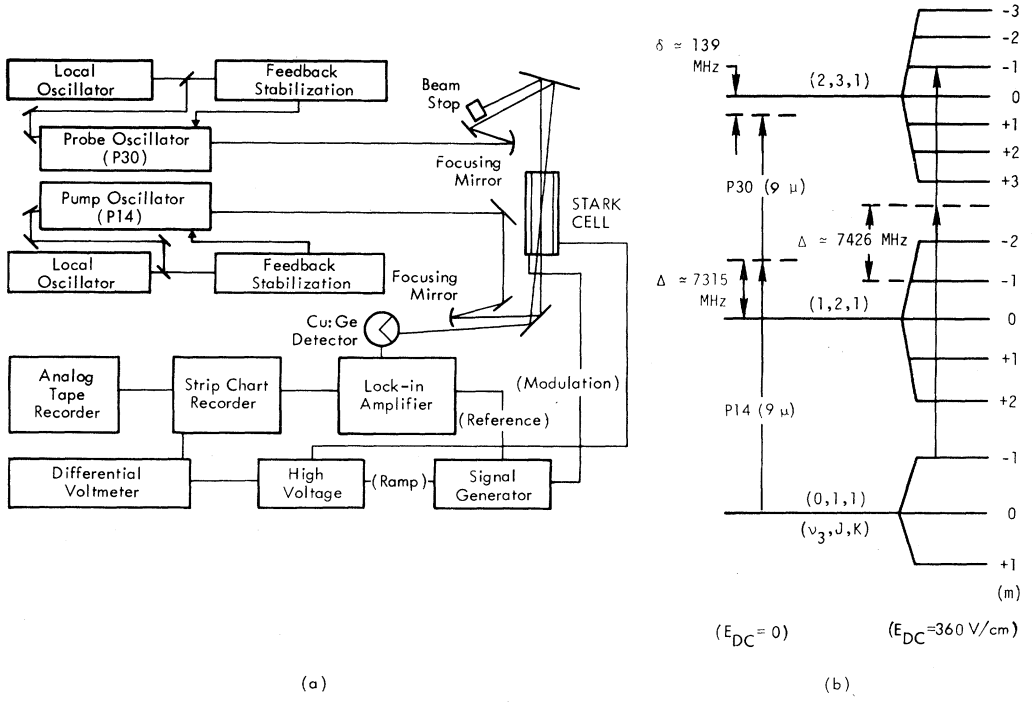

FIG. 1. (a) Schematic diagram of the experimental apparatus. (b) Stark energy diagram for the double parallel-polarization ($\Delta M = 0$) two-photon transition in the ν_3 bands of $^{12}CH_3F$.

allowed transitions for this parallel band are governed by the selection rules $\Delta J = \pm 1$, $\Delta K = 0$, and $\Delta M = 0, \pm 1$, depending on the polarization of the laser radiation field and the dc Stark field.

From the general theory of two-photon absorption,[3] one can calculate the absorption cross section between the ground state g and the excited state f for light at a probe frequency ν_2 induced by light at a pump frequency ν_1 from the following expression:

$$\sigma(\nu_2) = (2\pi)^3 I_1 \nu_2 |P_{fg}|^2 g(\nu_1 + \nu_2)/\hbar c^2, \quad (1)$$

where I_1 is the intensity of the pump radiation field, $g(\nu_1 + \nu_2)$ is the normalized line-shape function for the transition, and $P_{fg} = \langle f | \hat{\epsilon} \cdot \mu | n \rangle \langle n | \hat{\epsilon} \cdot \mu | g \rangle / (E_n - h\nu_1)$ for one dominant intermediate state. Polarization effects between the radiation fields and the Stark field ($\Delta M = 0$ or ± 1) play an important role in the direction-cosine matrix elements of P_{fg}. From tabulated expressions for the matrix elements of symmetric-top molecules,[4] it is found that the best enhancement occurs for the parallel-parallel case of[5] $(1, 1, -1) \rightarrow (3, 1, -1)$ with $(2, 1, -1)$ constituting the intermediate state. By making use of the opposed-beam technique[6] and for the experimental conditions described below, it is estimated that about 1×10^{-6} of the probe beam intensity should be absorbed for this case. This estimate is in agreement with measured signal intensities.

A block diagram of the experiment is given in Fig. 1(a). Two stable CO_2 lasers (labeled pump and probe oscillators) are locked to a specific frequency within their gain profile on their respective lines (9 μm, $P14$, and 9 μm, $P30$) via a local-oscillator heterodyning feedback system.[7] The output beams are then propagated through the Stark cell in opposite directions. Care is taken to maximize the overlap region in the Stark cell and yet ensure sufficient exit offset to separate the two beams. Both laser radiation fields are linearly polarized parallel to the dc Stark field and focused to a beam waist of 0.63 mm at the center of the cell. Typical pump beam intensities were ~375 W/cm^2.

The experiment consists of introducing a quantity of $^{12}CH_3F$ (approximately 5–150 mTorr) into the Stark cell and detecting the small amount of absorption of the probe beam by observing the output of a helium-cooled Cu:Ge detector and lockin amplifier system. The resonance is swept through by applying a ramp voltage (168–188 V) to the top plate of the cell via a biased 0–2000-V Kepco operational amplifier and a signal generator. The two-photon transition is thus Stark tuned from 130–146 MHz. A small sinusoidal modulating electric field of $\omega \sim 6$ kHz is applied to the bottom plate of the cell. After passing through the cell the probe beam is detected synchronously at the modulation frequency ω by an Ithaco model 391 lockin amplifier. The resulting signal is then recorded on magnetic tape for subsequent numerical reduction.

A sample of the data taken using this experimental arrangement is given in Fig. 2. The dark line is the actual data taken during the experiment. Note that there is no Doppler background due to separate beam two-photon absorption since the frequencies $2\nu_1$ and $2\nu_2$ are several hundred Doppler widths off the two-photon resonance. Since a large modulation voltage is needed for good signal-to-noise ratio, the observed resonance is broader than the true resonance. This modulation broadening is taken into account by computer fitting the observed data with Lorentzian linewidth expressions given by Smith.[8] This fit is the dotted line in Fig. 2. The true width of the resonance was derived from one of the parameters in the fitting code. The code was checked by taking data at the same pressure using different modulation amplitudes. All true widths derived from this code were within 80 kHz of their average. Additional broadening mechanisms[9] such as the transit-time effect, op-

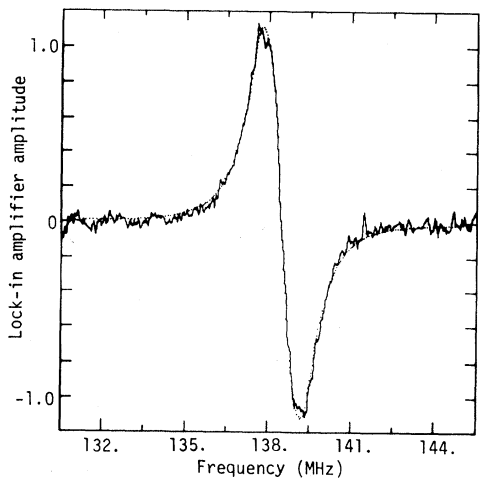

FIG. 2. Two-photon absorption observed for the selected transition of Fig. 1(b) using the apparatus of Fig. 1(a). The probe oscillator ($P30$, 9.4 μm) and the pump oscillator ($P14$, 9.4 μm) were locked 1 MHz below and above line center, respectively. $^{12}CH_3F$ pressure was 20 mTorr. Modulation voltage was 2 V peak to peak. Trace sweep time was 1.5 MHz/min. Data shown are a computer average of two consecutive runs.

tical Stark broadening, and power broadening are estimated to be less than 100 kHz and hence neglected in this analysis.

Figure 3 shows the true full width at half-maximum (FWHM) versus pressure. These linewidths are a convolution of the residual Doppler width[9] and the pressure-broadened width. Using a calculated residual Doppler width of 940 kHz and from tabulated values for the plasma dispersion function,[10] we have plotted the deconvolved values (shown by squares) for the homogeneous contribution. From this plot we determine a pressure-broadening coefficient $\Delta\nu_p = 41.3 \pm 1.0$ MHz/Torr. Since the dominant term in the collisional interaction is long-range dipole-dipole forces, we expect that the broadening mechanisms will be associated with those processes which transfer angular momentum.[11] These mechanisms are of the energy-changing (T_1) type and include molecular reorientation and rotational transitions. The former corresponds to a tipping of the angular momentum vector (J) between the various m states (which in our case are no longer degenerate) without a change in its magnitude[12]; the latter introduces a change in the magnitude of J. For collisions involving rare-gas perturbers, the intermolecular forces will differ significantly. As an example, the pressure-broadening coefficient for He + $^{12}CH_3F$ is found to be $\Delta\nu_p = 5.0 \pm 0.5$ MHz/Torr.

We also observe a "blue" pressure shift of $\Delta\nu_s$ 2.1 ± 0.1 MHz/Torr in the center frequency of the resonance as seen in Fig. 3. The average resonance frequency is determined by the difference

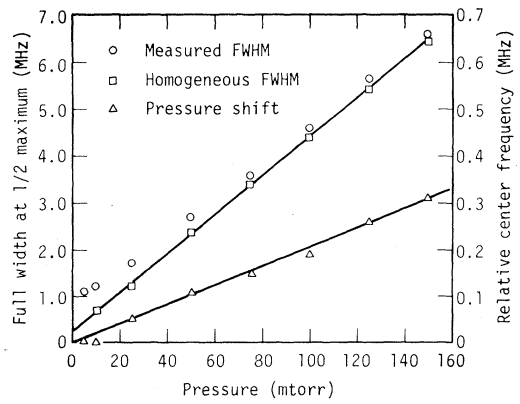

FIG. 3. Pressure-broadening ($\Delta\nu_p = 41.3 \pm 1.0$ MHz/Torr) and pressure-shift ($\Delta\nu_s = 2.1 \pm 0.1$ MHz/Torr) data for the $(0,1,1,-1) \rightarrow (1,2,1,-1) \rightarrow (2,3,1,-1)$ transition in $^{12}CH_3F$. $(0,1,1,-1)$ denotes $\nu_3 = 0$, $J = 1$, $K = 1$, $M = -1$. The zero-pressure resonant frequency is $\delta = 138.80$ MHz [see Fig. 1(b)].

in the collisional perturbations in the initial and final states.[13] In our case the lower-state dipole moment is fixed in space ($J = 1, K = 1$) whereas the upper-state dipole moment is rapidly spinning ($J = 3, K = 1$). Consequently, the difference in the interaction between the perturbing molecule and these internal motions should lead to a pressure shift as is experimentally observed.

The zero-pressure center-frequency difference is measured to be $\delta = 138.8 \pm 0.1$ MHz [see Fig. 1(b)] and is limited by the accuracy of the plate spacing and the upper- and lower-state dipole moments. The plate spacing is calibrated by varying the locked offset frequencies of both the pump and probe lasers from their respective line centers and observing the Stark voltage required to shift the transition into resonance. Differences in these energy shifts are then calculated using values for the dipole moments taken from Ref. 2. This gave us a plate spacing of 0.496 48 $\pm$ 0.000 10 which is within the experimental error of the measured value.

In conclusion, we have demonstrated the technique of opposite-direction two-photon absorption for the first time in a molecular species using two fixed-frequency optical fields in combination with molecular Stark tuning. We report a measured self-broadening coefficient of $\Delta\nu_p = 41.3 \pm 1.0$ MHz/Torr and a resonant frequency shift of $\Delta\nu_s = 2.1 \pm 0.1$ MHz/Torr for the previously described transition. Signals have been observed using different polarizations ($\Delta m = \pm 1$) and are in accord with strengths predicted by the appropriate matrix elements. It is expected that the small residual Doppler width (~1 MHz) associated with this technique will provide increased resolution to investigate the finer details of molecular structure. In addition, it may be noted that resonant enhancement associated with intermediate-state Stark tuning greatly increases the absorption cross section thereby permitting efficient up- and down-conversion schemes.[14]

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*Major, U. S. Army Research Office, Box CM, Duke Station, Durham, N. C., with duty station Lawrence Livermore Laboratory, Livermore, Calif. 94550.

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Observation of the $E2$ Nuclear Resonance Effect in Pionic Cadmium*

J. N. Bradbury and M. Leon
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544

and

H. Daniel
University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87544, and Technical University of Munich,† Munich, Germany

and

J. J. Reidy‡
University of Mississippi, University, Mississippi 38677
(Received 2 December 1974)

Nuclear resonance effects in mesonic atoms result from near degeneracy of nuclear excitation and atomic de-excitation energies. The $E2$ nuclear resonance effect was observed in pionic cadmium by comparing selected pionic x-ray intensity ratios from ^{112}Cd with those from ^{111}Cd. The effect for hadronic atoms is now unambiguously established and the results are in close agreement with the theoretical predictions.

Nuclear resonance effects in mesonic atoms result from "accidental" near degeneracy of nuclear excitation and atomic de-excitation energies. Given such an energy matching, even a relatively weak coupling—such as that provided by the electric quadrupole moment of the nucleus—can produce significant configuration mixing. Thus, in effect, the mesonic atom de-excites by exciting the nucleus. It has recently been pointed out[1,2] that this $E2$ nuclear resonance effect should be easy to observe in a few *hadronic* atoms: those for which the absorption of the hadron by the excited nucleus weakens one or two hadronic x-ray line intensities relative to the intensities from another isotope of the same element.[3] This effect is intrinsically interesting and also provides an important test of our knowledge of the hadron-nucleus interaction.

In this Letter we report the observation of the nuclear resonance effect in pionic cadmium. While this effect has been seen[4] in muonic Bi and Tl, this is, to our knowledge, the first such observation for hadronic atoms.

For pionic cadmium the predicted[5] $5g \rightarrow 3d$ (complex) atomic energy difference is $618.8 + i1.0$ keV, while both ^{112}Cd and ^{111}Cd have $E2$ excitable states near that energy: 617.4 ± 0.3[6] and 619.9 ± 0.3 keV,[7] respectively. Thus pionic atoms of these isotopes are choice candidates for exhibiting the nuclear resonance effect; in each, the induced