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Stimulated Raman pumping of C_2^- probed via resonant two-photon detachment

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Abstract

We demonstrate for the first time that stimulated Raman pumping (SRP) can be used to vibrationally excite gas-phase negative ions. Results are presented for C_2^-, in which stimulated Raman pumping excites a rotationally resolved transition between the $v = 0$ and $v = 1$ levels of the ground $^2\Sigma_g^+$ state; this excitation is monitored by resonant two-photon detachment through the excited B $^2\Sigma_u^+$ state. At least 35% conversion to the $v = 1$ level was achieved in this study. It is expected that this method is quite generally applicable and will provide an excellent tool for the study of the vibrational spectroscopy of negative ions.

1. Introduction

The vibrational spectroscopy of gas phase anions remains largely unexplored. In most experimental environments, the anion density is quite low, so one requires an extremely sensitive spectroscopic technique to study these species. Velocity-modulated infrared absorption spectroscopy [1], which has proved so useful in studying positive ions, has been applied successfully to only a handful of negative ions [2–5]. A very different method, vibrational autodetachment spectroscopy, was used to obtain high resolution infrared spectra of mass-selected ion beams of NH^- [6] and HNO^- [7]. This technique can detect much lower ion densities than velocity-modulated absorption, and it has the advantage of mass-selectivity, but it relies on excitation to a vibrationally excited state above the detachment threshold and is therefore only applicable to a very limited number of systems. Vibrational frequencies of negative ions can also be obtained through hot-band and sequence-band transitions in various electronic spectroscopy experiments, such as electronic autodetachment spectroscopy [8], anion zero electron kinetic energy spectroscopy [9,10], and, at considerably lower resolution, anion photoelectron spectroscopy [11]. However, one is usually limited to the observation of a few low-frequency modes in these studies. It is clearly of interest to develop an experimental method which combines generality with high sensitivity, good resolution, and mass selectivity. Stimulated Raman pumping combined with photodetachment offers considerable promise as such a tech-

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nique. In this Letter, we present the first application of stimulated Raman pumping (SRP) to the vibrational spectroscopy of negative ions.

In a SRP experiment, vibrational excitation of a molecular species is achieved through interaction with two laser beams at frequencies ω_1 and ω_2, where $\omega_1 - \omega_2$ is equal to a vibrational transition of the molecule [12]. Esherick and co-workers [13,14] were the first to demonstrate that SRP, when combined with resonantly enhanced multiphoton ionization (REMPI), was sufficiently sensitive to generate and detect vibrational excitation of neutral molecules in a molecular beam. More recently, Felker and co-workers [15] have used this combination of methods with considerable success in studying the vibrational spectroscopy of van der Waals clusters in a beam.

These experiments suggest the possibility of combining SRP with photodetachment as a means of studying negative ions. However, negative ions are usually found in very low concentrations, typically 10^4–10^6 cm^{-3} in a pulsed, mass-selected ion beam. This is several orders of magnitude less than the concentration of van der Waals clusters usually achieved in a molecular beam, raising the question of whether or not sufficient population transfer can be induced in a negative ion beam by SRP to be observable. Recently, Kristensen et al. [16] have used photodetachment to detect stimulated Raman pumping of an *electronic* transition in the Te^- anion, suggesting that the analogous vibrational excitation experiment might indeed be feasible.

In this Letter, SRP of the C_2^- anion is demonstrated. The SRP process is monitored by resonant two-photon detachment (R2PD), the negative ion analog of REMPI. Fig. 1 schematically shows the energy levels and laser pulses involved in the pump and probe process. Stimulated Raman pumping is achieved by a pair of laser pulses overlapping in time and space, indicated by ω_1 (pump pulse) and ω_2 (Stokes pulse). The ions are then selectively photodetached via R2PD by the probe pulse, ω_3. The experiment can be carried out in either a depletion or gain mode. The electron depletion experiment is illustrated in Fig. 1. Here, the R2PD probe laser is tuned to a transition from the $v = 0$ level of the anion. A depletion of $v = 0$ population, and hence electron signal, will be observed when the energy

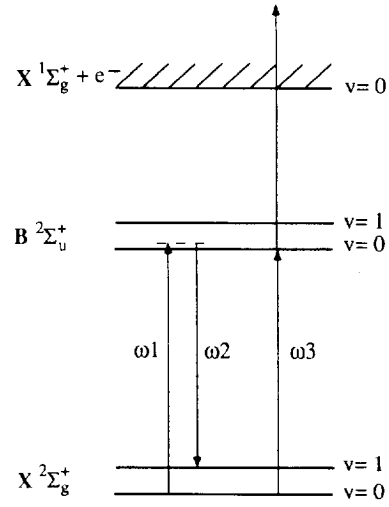

Fig. 1. Energy level diagram illustrating the excitation and detection scheme used in the present experiments. The pump ω_1 and Stokes ω_2 pulses drive the stimulated Raman transition. The probe pulse ω_3 monitors the population in $v = 0$ via resonantly enhanced two photon detachment (R2PD).

difference between the pump and Stokes beam is resonant with the $v = 0 \rightarrow v = 1$ transition. In the analogous gain experiment (not shown), the probe laser is tuned to a transition originating from the $v = 1$ level of the anion, monitoring an increase in detachment from this level as the energy difference in pump and Stokes beam becomes resonant. As our ions are initially in their vibrational ground state, the gain experiment is a background-free technique.

We have selected C_2^- as a test system for various reasons. In the first place, C_2^- has a large Raman cross section. We have performed ab initio calculations using the GAUSSIAN 92 package which indicate that the C_2^- Raman cross section is more than one order of magnitude more intense than that of the 3074 cm^{-1} mode of benzene; the latter is a strong Raman transition [17] which was exploited by Felker et al. [15] in their cluster studies. Moreover, C_2^- has an electronically excited state, the B $^2\Sigma_u^+$ state, below the detachment threshold which can be optically excited from the ground X $^2\Sigma_g^+$ state. This allows us to use R2PD as a probe of the population, directly analogous to the REMPI detected SRP technique which has been so successful for neutral species. The C_2^- B $^2\Sigma_u^+ \leftarrow$ X $^2\Sigma_g^+$ band system was first observed by Herzberg and Lagerqvist [18], and their

assignment was later confirmed by Lineberger and Patterson [19] in a R2PD study of C_2^-. Thanks to these studies, the vibrational and rotational constants of C_2^- are sufficiently well-characterized so that the wavelengths necessary for SRP and R2PD are accurately known.

2. Experimental

The experimental set up has been described elsewhere [20], with the exception of the laser system used for the SRP process. The apparatus was originally designed for anion zero electron kinetic energy spectroscopy, but it can also be used to measure total photodetachment cross sections. The apparatus is used in this latter mode for the work described here.

Briefly, a cold beam of C_2^- ions is generated by expanding a pulsed supersonic expansion of a gas mixture (5% C_2H_2, 3% CO_2, 92% He) through a pulsed electrical discharge [21]. The negative ions are accelerated to 1 keV and mass selected in a time-of-flight mass spectrometer. The mass-selected ion packet has a diameter of ≈ 1 mm and is temporally focused to a pulse duration of ≈ 40 ns fwhm at the point where it is crossed by the laser beams. The resulting photoelectrons are extracted by a weak (10 V/cm) field perpendicular to the ion beam direction and are collected by a 40 mm diameter dual microchannel plate detector. Gated detection insures that only those electrons produced within a specific 35 ns wide time interval are accumulated.

The pump and Stokes beams for the SRP process are provided by an injection-seeded YAG-pumped dye laser system (Continuum Powerlite 9020, and Continuum ND6000). The output of the YAG laser is frequency doubled to 532 nm (7 ns pulse duration, up to 900 mJ/pulse at 532 nm). A beam splitter inside the dye laser splits off a fraction ($\approx 20\%$) of the 532 nm light, which is used as the pump beam in the SRP experiment. The dye laser, operated using rhodamine 610 dye, provides the tunable Stokes beam (7 ns pulse duration, up to 300 mJ/pulse, bandwidth 0.07 cm^{-1}). As the pump and Stokes beam originate from the same YAG pulse, temporal overlap is achieved as long as the path lengths of the two beams are equal. The beams are spatially overlapped by using a dichroic mirror and are loosely focused inside the vacuum chamber to a beam waist of ≈ 1 mm. The probe beam is provided by an excimer pumped pulsed dye laser system (Lambda Physik, 25 ns pulse duration, 1–25 mJ/pulse, bandwidth ≈ 0.1 cm^{-1}), which is counterpropagating along the direction of the SRP beams. This dye laser is operated using coumarin 540A. The wavelength of both dye lasers was calibrated using an I_2 absorption cell. Once this is done, the wavelength of the frequency doubled output of the YAG laser is determined by coherent anti-Stokes Raman Scattering (CARS) on atmospheric O_2 and N_2 [22].

Two types of experiment were performed. Firstly, the R2PD resonances were located in one- and two-color scans, in which the probe laser, ω_3, is scanned. In the two-color scans either the pump or Stokes beam was temporally overlapped with the probe laser to enhance the electron signal. Secondly, we performed SRP experiments, in which vibrational excitation of the ions was monitored by R2PD. In these experiments the spatially and temporally overlapped pump and Stokes pulses intersect the ion packet. After a variable time delay (≈ 0–50 ns), the negative ions are selectively photodetached by the probe laser which is tuned to a resonance of interest. The SRP spectrum is obtained by tuning the Stokes laser and monitoring either gain or depletion of the electron signal (see Fig. 1).

Temporal separation of the pump and probe laser pulses serves to eliminate unwanted multiphoton processes. As our ion packet is moving at 1 keV, the temporal separation of the laser pulses implies that the pulses have to be appropriately separated spatially in order for the laser pulses to intersect the same ion packet. The SRP signal was optimized by carefully adjusting the firing times and spatial separation of the pump and probe pulses.

3. Results and discussion

Fig. 2 shows the rotationally resolved two-color R2PD spectrum for the $B\,^2\Sigma_u^+(v=0) \leftarrow X\,^2\Sigma_g^+$ $(v=0)$ transition. This was obtained by scanning the probe laser ω_3 (1 mJ/pulse) which was temporally overlapped with the pump beam at 532 nm (60 mJ/pulse) while the Stokes beam was blocked. In this spectrum, the B ← X bound–bound transition

is excited by ω_3, while both the weak pump pulse and the more intense pump pulse detach the electronically excited anions through a considerably weaker bound → free transition. The width of the lines (≈ 1 cm^{-1} fwhm) exceeds that of the probe laser bandwidth (≈ 0.1 cm^{-1}) due to a slight power broadening of the $B\,^2\Sigma_u^+ \leftarrow X\,^2\Sigma_g^+$ transition. A one-color R2PD spectrum can be obtained simply by blocking the pump beam. This results in a substantial drop in signal since the photodetachment transition is not being pumped nearly as hard.

The assignment to the rotational transitions is indicated in Fig. 2. Only P ($\Delta N = -1$) and R ($\Delta N = +1$) branches are observed, as expected for a Σ–Σ transition. Only even rotational levels are observed due to nuclear spin statistics. The rotational distribution is non-Boltzmann, as often is observed in supersonic expansions. The best fit is obtained for a temperature of ≈ 80 K. No transitions originating from vibrationally excited ions are observed, indicating that the ions are vibrationally cold.

Figs. 3a and 3b show stimulated Raman spectra in the depletion and gain mode, respectively. In both spectra, the probe pulse ω_3 (1.8 mJ/pulse) is delayed 40 ns with respect to the pump and Stokes pulse pair, ω_1 (60 mJ/pulse) and ω_2 (40 mJ/pulse). In Fig. 3a, the probe laser is tuned to the $B\,^2\Sigma_u^+(v=0) \leftarrow X\,^2\Sigma_g^+(v=0)$ R(2) transition while ω_2 is scanned. When $\omega_1 - \omega_2$ equals the energy of the $X\,^2\Sigma_g^+(v=1) \leftarrow (v=0)$ Q(2) Raman transition, the $v=0$, $N=2$ population is depleted, leading to a decrease in photodetachment via the probe pulse.

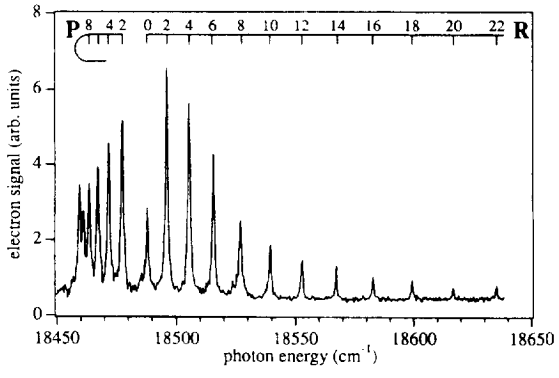

Fig. 2. Resonant two photon detachment (R2PD) scan of the C_2^- $X\,^2\Sigma_g^+(v=0) \rightarrow B\,^2\Sigma_u^+(v=0)$ transition. Assignment of the rotational transitions is indicated in the figure.

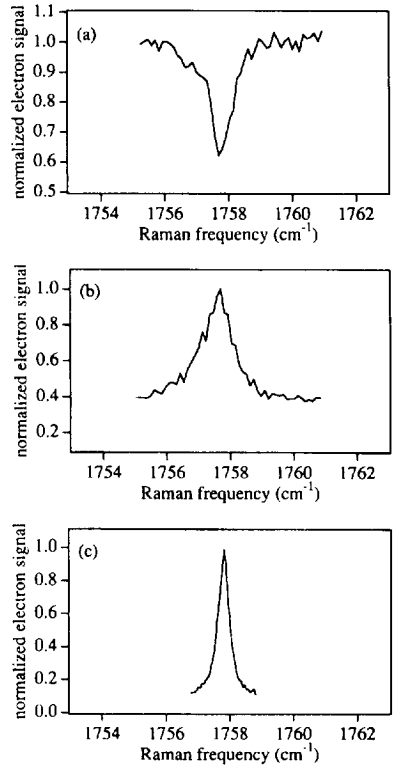

Fig. 3. (a) Electron depletion stimulated Raman spectrum of C_2^-. The pump and probe pulses are separated by 40 ns. The x-axis energy scale is obtained by subtracting the photon energy of the Stokes laser from that of the pump laser. The probe laser is tuned to the $B\,^2\Sigma_u^+(v=0) \leftarrow X\,^2\Sigma_g^+(v=0)$ R(2) transition. The dip corresponds to the $X\,^2\Sigma_g^+(v=1) \leftarrow (v=0)$ Q(2) Raman transition. (b) Electron gain stimulated Raman spectrum of C_2^-. The pump and probe pulses are separated by 40 ns. The probe laser is tuned to the $B\,^2\Sigma_u^+(v=1) \leftarrow X\,^2\Sigma_g^+(v=1)$ R(2) transition. The peak corresponds to the same Raman transition in (a). (c) Electron gain stimulated Raman spectrum of C_2^- for temporally overlapping pump and probe pulses. The probe laser is tuned to the $B\,^2\Sigma_u^+(v=1) \leftarrow X\,^2\Sigma_g^+(v=1)$ R(2) transition. The peak corresponds to the same Raman transition in (a).

The width of the resulting peak is 0.7 cm^{-1} fwhm, and the magnitude of the depletion is 35%. With this degree of depletion, saturation effects leading to line broadening might be expected. This is consistent with the observed linewidth, which is significantly wider than the convoluted linewidth of the SRP pulses (≈ 0.1 cm^{-1}).

In Fig. 3b, the probe laser is fixed on the $B\,^2\Sigma_u^+(v=1) \leftarrow X\,^2\Sigma_g^+(v=1)$ R(2) transition, monitoring a gain in population of the $v=1$, $N=2$ level as ω_2 is scanned. There is essentially no signal

unless $\omega_1 - \omega_2$ matches the $v = 0 \rightarrow 1$ Q(2) Raman transition in the $X\,^2\Sigma_g^+$ state, resulting in a sharp peak on top of little background. Although the background-free aspect of the gain experiment is appealing, it is less generally useful than the depletion experiment because one must know the vibrational frequencies of the upper and lower electronic states prior to the experiment in order to determine where to set the probe laser for R2PD.

An alternative mode of performing the SRP experiment is to fire all lasers simultaneously. The advantage of this is that detachment can now occur through two-color R2PD with the second photon coming from the intense pump or Stokes pulse, so it is more efficient than in the case of temporally separated pulses where only one-color R2PD can occur. Fig. 3c shows the gain experiment for temporally overlapped laser pulses. The pump and Stokes lasers are operating at 33 and 21 mJ/pulse, respectively. The probe laser, tuned to the same resonance as for the scan presented in Fig. 3b, is now operated at 0.8 mJ/pulse. The signal-to-noise is noticeably better than in Figs. 3a or 3b, even though all three laser pulse energies are lower. The reduction of the pump and Stokes pulse energies yields a narrower peak, as well: 0.35 cm^{-1} at fwhm.

For C_2^-, the depletion experiment did not work under conditions of temporally overlapped pulses. The failure of the depletion experiment can be rationalized by assuming that the R2PD cross section is greater than the SRP cross section, which is quite reasonable since the R2PD process consists of two sequential one-photon steps, while SRP is a true two-photon process. In the depletion experiment, the probe laser is tuned to a resonance originating from $X\,^2\Sigma_g^+(v = 0)$, so R2PD quickly depletes the ground state population. With pump and probe pulses overlapping, the fast R2PD process will dominate and little population is transferred to $v = 1$ by SRP, so no electron depletion is observed. By temporally delaying the probe laser, the SRP process can occur without competing with the R2PD process. In the gain experiment, the probe laser is tuned to a resonance originating in $X\,^2\Sigma_g^+(v = 1)$, a level which has no initial population. In this case no detachment occurs *unless* the SRP process takes place first. Therefore, the SRP process can take place irrespective of the presence of the probe pulse.

In all modes of operation, only the Q-branch ($\Delta N = 0$) Raman transition was observed experiments. O ($\Delta N = -2$) and S-branch ($\Delta N = +2$) transitions are also allowed, but the Q-branch transition is generally much more intense. The position of the dip and peak (1757.8 ± 0.3 cm^{-1}) are in excellent agreement with the known vibrational and rotational level spacing in the $X\,^2\Sigma_g^+$ state [18,19].

4. Prospects for future work

Having demonstrated that vibrational SRP spectroscopy on a negative ion is feasible, we now consider how general it might be. C_2^- was particularly attractive because of its large Raman cross section and its optically accessible electronic state below the detachment threshold, enabling us to probe the SRP process via rotationally resolved R2PD. The Raman cross-section is further enhanced by the fact that the 'virtual-state' at 532 nm accessed in the Raman process lies close to the optically allowed B state (origin at 540 nm).

Unfortunately, most negative ions do not optically accessible excited states below their detachment threshold. However, there are certainly a number of molecular and cluster anions with excited valence or dipole-bound states which could be studied by the method described in this Letter [8,23,24]. The larger carbon cluster anions are of particular interest, since very recent experiments in our group and by Maier and co-workers [25] have shown that C_4^-, C_6^- and C_8^- have optically allowed electronic states below the detachment threshold. On the other hand, the large Raman cross section calculated for C_2^- appears to be a more general property of negative ions. We have performed ab initio calculations using GAUSSIAN 92 which indicate that quite a few anions, including the above mentioned carbon clusters, have Raman cross sections of the same order of magnitude as C_2^-.

One way to apply SRP to a larger number of anions is to use a one-photon detachment rather than R2PD as a probe of vibrational excitation. In this detection scheme, the population in $v = 1$ is monitored by tuning the probe laser just short of the detachment threshold, detecting only population in vibrationally excited levels of the anion. This is

analogous to the scheme used in the Raman-type experiment on the Te anion [16]. As all ions are initially in their vibrational ground state, this is a background free technique. Such a scheme is energetically feasible for most negative ions, since electron affinities are generally smaller than 5 eV. This method of detection does require that the Franck–Condon factor for the ($v = 1$) anion to ($v = 0$) neutral transition is appreciable and that the detachment cross section near threshold is reasonably large. The latter requirement is met for s-wave photodetachment [26]. These requirements are satisfied for a fair number of anions, and we hope to implement this detection scheme shortly.

The results presented in this paper show that SRP can be used to vibrationally excite a large fractions of population in a given vibration–rotation level. For heavier molecules than C_2^-, the rotational constant will be smaller, leading to a closely spaced Q-branch, allowing us to pump a sizable fraction of the *total* anion population to a vibrationally excited state. This provides us with the exciting prospect of studying photoelectron spectroscopy of anions prepared in a particular vibrationally excited state, with the ultimate goal of extending our efforts to characterize the transition state of neutral reactions. We have demonstrated that a neutral transition state can be investigated by photoelectron spectroscopy of a suitable precursor anion [27]. Up until now, we have been limited to studying the region of the potential energy surface which has good Franck–Condon overlap with the ground vibrational state of the anion. We can explore a much larger region of the neutral potential energy surface by *vibrationally exciting* the anions prior to photodetachment. By exciting specific vibrational modes of the anion we can probe different regions of the potential energy surface in a systematic way. The experiments presented in this Letter form an important step towards this goal.

5. Conclusions

We have demonstrated that one can study the vibration–rotation spectroscopy of a negative ion, C_2^-, by exciting the ion with stimulated Raman pumping and probing the excitation with resonant two-photon detachment. The stimulated Raman pumping was shown to be very efficient even with relatively loosely focused pump and Stokes laser pulses. This is presumably because of the large Raman cross section for C_2^-, a property common to many other negative ions. We expect that stimulated Raman pumping combined with various photodetachment schemes will be applicable to a large number of anions, thereby providing a novel tool for the study of the vibrational spectroscopy of negative ions and negative ion clusters.

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