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Vibrational spectroscopy of anions by stimulated Raman pumping–photoelectron spectroscopy

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Abstract

The first demonstration of a technique for the vibrational spectroscopy of anions, stimulated Raman pumping-anion photoelectron spectroscopy is reported. It combines the high spectral resolution of stimulated Raman pumping with the high detection efficiency, mass-selectivity, and wide applicability of anion photoelectron spectroscopy. The vibrational spectrum of a test system, C_2^-, is recorded and the frequency of the $1 \leftarrow 0$ vibrational transition is determined to be 1757.8 ± 0.1 cm^{-1}. The *Q*-branch is partially rotationally resolved. © 2000 Published by Elsevier Science B.V.

1. Introduction

Measurement of the vibrational spectra of negative ions has been a challenging problem in molecular spectroscopy for many years. In nearly all experimental environments, negative ions are far less abundant than neutral species or positive ions, so high selectivity and sensitivity are required for any spectroscopic method [1]. Velocity-modulated infrared (IR) spectroscopy has been used to obtain rotationally resolved IR absorption spectra for a handful of negative ions [2]. Alternatively, experiments can be performed on mass-selected ion beams. This removes any doubt concerning the identity of the species under study, but because of the very low ion densities in such experiments (typically 10^4 ions/cm^3 or less), the high sensitivity of action spectroscopy is required. In the past, vibrational excitation has been monitored by autodetachment [3] or by predissociation [4–7], both of which produce charged particles that can be detected with nearly unit efficiency. However, these methods require that the vibrational energy of the excited ion exceeds the electron affinity or the dissociation energy of the weakest bond.

In this Letter we describe an experimental approach to the vibrational spectroscopy of mass-selected negative ions which is independent of these energetic constraints – stimulated Raman pumping–photoelectron spectroscopy (SRP-PES). In this experiment, the negative ion is vibrationally excited by stimulated Raman pumping (SRP), and this excitation is detected through the appearance of new features in its photoelectron spectrum.

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SRP was first observed in 1962 [8]; since then, it has been used to study such varied topics as energy transfer [9], spectroscopy [10,11], reaction dynamics [12], and even Bose–Einstein condensation [13]. It occurs when two intense light beams interact with a sample; when the difference in the frequencies of the beams matches a transition of the sample, energy is absorbed and the sample is excited [14]. By tradition, these beams are referred to as the ‘pump’ and ‘Stokes’ beams, where the pump beam is at a higher frequency (see Fig. 1). SRP can be used to pump molecules efficiently over a wide frequency range, extending down to tens of wavenumbers; in contrast, below 2000 cm^{-1} IR laser excitation is either not very efficient or not continuously tunable.

Stimulated Raman pumping has been used with great success in studies of neutral molecules and clusters by monitoring either the ground or vibrationally excited population through resonant multiphoton ionization [11]. A similar method has been demonstrated for the negative ions Te^- [15] and C_2^- [16], using resonant two-photon detachment (R2PD) through an excited electronic state of the anion. However, for this experiment the negative ion must have a bound electronic state below the detachment threshold, a relatively rare situation.

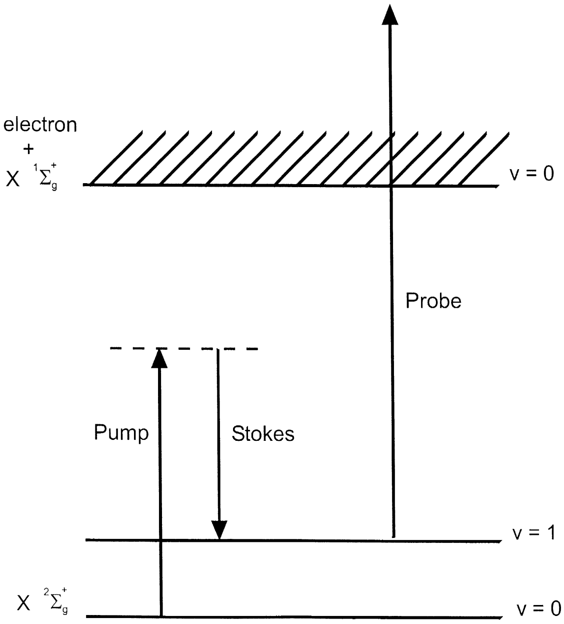

Fig. 1. Energy level diagram for stimulated Raman pumping–photoelectron spectroscopy of C_∂^-. The pump and Stokes pulses drive the SRP transition, and the probe pulse detaches the electron.

We have decided to combine SRP with direct single-photon detachment. After the two Raman beams vibrationally excite the anion, a fixed-frequency photon (the ‘probe’ beam) detaches an electron, and the kinetic energies of the resulting electrons are determined by time of flight (see Fig. 1). Because ions that are vibrationally excited by SRP have additional internal energy, electrons detached from these ions can appear as hot bands at higher electron kinetic energies than are seen from ground state detachment. By recording the integrated intensity in this hot-band region, we can monitor the vibrationally excited population induced by SRP. This experiment requires that the collection efficiency of the photoelectrons be very high, as we need to measure the photoelectron spectrum at each Stokes wavelength while searching for hot bands. This condition is satisfied in our experiment by the use of a ‘magnetic bottle’ electron energy analyzer [17].

We have chosen to study the dicarbon anion, C_2^-, in order to demonstrate that SRP can be combined with anion PES. Because C_2^- is one of the few anions with electronically excited states below its detachment threshold [18,19], its gas-phase spectroscopy has been studied in detail [20]. Also, we have already demonstrated that a large fraction of the population of a given rotational level of C_2^- can be transferred to its vibrationally excited state by SRP [16]. C_∂^- therefore seems a natural system on which to test SRP-PES.

2. Experimental

The experimental apparatus is a modified version of an instrument reported previously [21]. The ion source and mass spectrometer have not changed, and so will be described only briefly. The laser system, ion-laser interaction region, and signal detection scheme are quite different and will be described in more detail.

Ions are generated by supersonic expansion of a mixture of 2% ethyne and 0.5% carbon dioxide in neon through a pulsed valve at 20 Hz. At the end of the valve is a pulsed electrical discharge (which generates cations, anions, and neutrals) along with a 1 keV electron beam, which stabilizes the discharge plasma. The resulting negative ions are skimmed and accelerated across a potential difference of 600–1000 V. Mass selection of the ions occurs in a coaxial beam-modulation time-of-flight (TOF) mass spectrometer [22,23]. The ions then pass through several ion optics and are detected by a pair of microchannel plates, yielding a mass resolution of approximately 200.

In the interaction region, the ion packet of interest is crossed first by the pump and Stokes beams. The pump beam is provided by part of the output of a frequency-doubled injection-seeded Nd:YAG laser (Continuum Powerlite 9020, 532 nm, 0.003 cm^{-1} bandwidth, 7 ns pulse duration, 10–50 mJ/pulse). The Stokes beam is provided by a dye laser (Continuum ND6000, 0.1 cm^{-1} bandwidth, 7 ns pulse duration, 2–40 mJ/pulse) that is pumped by the balance of the output of the Nd:YAG laser. The Stokes beam is tunable over a range of 580–605 nm (Rhodamine 610 perchlorate dye, Exciton). The linearly polarized beams are spatially combined by a dichroic mirror and loosely focused to a 2 mm diameter spot at the interaction region, ensuring that the beams interact with the entire ion packet (approximately 1 mm in diameter); this gives fluences of 0.2–2 J cm^{-2} for the pump beam and 0.06–2 J cm^{-2} for the Stokes beam. The SRP beams are calibrated by a pulsed wavemeter (Burleigh WA-4500, ± 0.02 cm^{-1} accuracy).

The ions are photodetached approximately 25 ns after they interact with the SRP lasers. The photodetachment beam is provided by a frequency-quadrupled Nd:YAG laser (Continuum NY60B, 266 nm, (4.657 eV), 1 cm^{-1} bandwidth, 4 ns pulse duration, 4 mJ/pulse) focused to a 2 mm diameter spot.

The probe laser interacts with the ion packet at the focus of a magnetic bottle electron TOF energy analyzer [17]. In our design [24], a strong permanent magnet is placed just below the interaction region and a solenoid is wrapped around the electron TOF drift tube, which is located above the interaction region. The magnetic field decreases rapidly from approximately 70 mT at the interaction region to 2 mT in the drift tube. Because the rapidly diverging field lines at the interaction region map smoothly onto the field lines of the solenoid, this arrangement directs a large fraction of the ejected electrons onto the electron detector at the terminus of the drift tube. However, because the ion packet itself has a large velocity (90 km s^{-1} for C_2^-), electrons that are ejected with the same kinetic energy in the center of mass frame but in different directions can have significantly different arrival times at the detector. This results in a substantial broadening ('Doppler broadening') of the peaks in the photoelectron spectrum [25], particularly for light ions such as C_2^-. Typically 50–100 electrons are collected per laser shot.

Finally, the electron arrival times are recorded by a microchannel plate detector attached to an amplifier and then a digital oscilloscope (Tektronix TDS620B). The resulting spectra are downloaded to a personal computer, where they are converted from time-of-flight to electron kinetic energy. This conversion is calibrated by the photoelectron spectra of O_2^-, Cl^-, Br^-, and I^-.

We can perform two types of experiment on this apparatus. First, we can fix the Stokes laser frequency so that the SRP is resonant with a particular anion transition and measure the resulting photoelectron spectrum of the vibrationally excited anion. Second, we can scan the Stokes laser frequency and monitor the integrated intensity in the hot-band region (which must come from ions which have undergone SRP), and thus obtain the Raman spectrum of the ion.

3. Results and discussion

Fig. 2 shows the photoelectron spectrum of C_2^- taken with the stimulated Raman lasers either on- or off-resonance with the $Q(4)$ line of the $1 \leftarrow 0$ vibrational transition. As mentioned above, Doppler broadening causes the peaks due to transitions to different levels of the neutral molecule to broaden and overlap, making the spectrum somewhat congested. The expected peak positions seen in high-resolution anion photoelectron spectroscopy [26], along with the calculated Doppler-broadened peak widths, are given in Table 1. The spectrum observed here is completely consistent with those earlier results. In order to highlight the signal from the vibrationally

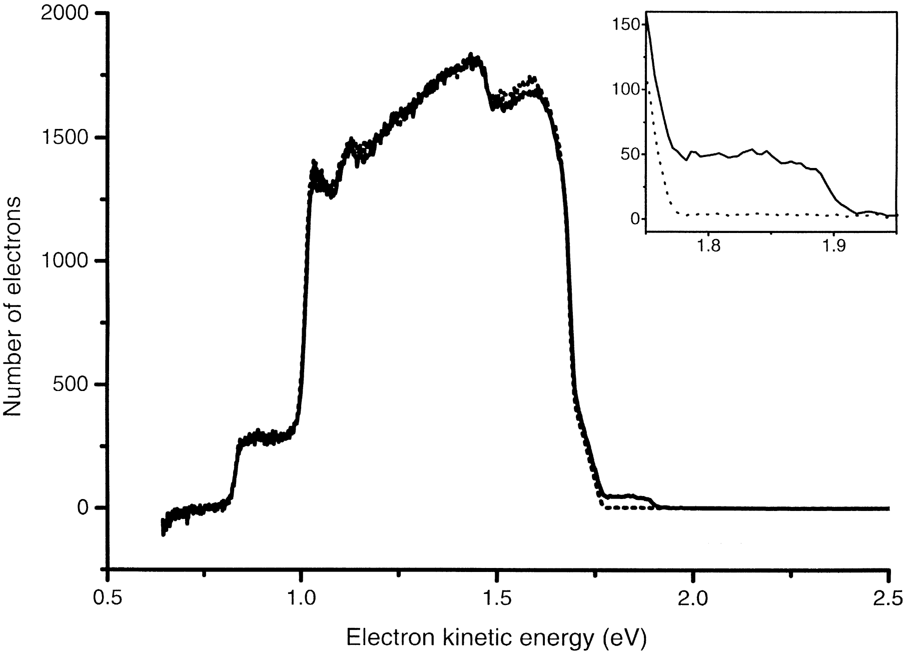

Fig. 2. SRP-PES spectrum of C_2^-. Solid line: experimental data when the SRP beams are resonant with the $Q(4)$ transition; dotted line: experimental data when the SRP beams are off-resonance. The inset shows an expanded view of the hot-band region. Each trace represents the sum of 25 000 laser shots after background subtraction. The Raman lasers are at high power (2 J cm^{-2} pump, 1 J cm^{-2} Stokes), and the probe laser photon energy is 4.657 eV. See Table 1 for peak assignments.

excited anions, the inset shows a magnified view of the high electron kinetic energy portion of the spectrum. Off-resonance, or with the SRP lasers blocked, a negligible fraction of the ions are vibrationally excited. When the lasers are on resonance, approximately 2000 electrons from the two $v''=1$ transitions listed in Table 1 appear in the hot-band region. (Note that Doppler broadening causes only a fraction of the electrons ejected from vibrationally excited anions to appear at high electron kinetic energies.) This corresponds to excitation of about 6% of the anions in the $(v''=0,\ J''=4)$ state to the $(v'=1,\ J'=4)$ state. Even the results of this relatively inefficient pumping process are clearly visible.

Table 1
Peak assignments for the anion photoelectron spectrum of C_2^-. The photon energy is 4.657 eV

Anion photoelectron transition (neutral ← anion)	Electron kinetic energy [a] (eV)	Doppler-broadened electron kinetic energy range [b] (eV)
$X^1\Sigma_g^+\ (v'=0) \leftarrow X^2\Sigma_g^+\ (v''=1)$	1.609	1.248–2.015
$a^3\Pi_u\ (v'=0) \leftarrow X^2\Sigma_g^+\ (v''=1)$	1.542	1.189–1.940
$X^1\Sigma_g^+\ (v'=0) \leftarrow X^2\Sigma_g^+\ (v''=0)$	1.384	1.051–1.763
$a^3\Pi_u\ (v'=0) \leftarrow X^2\Sigma_g^+\ (v''=0)$	1.310	0.987–1.679
$X^1\Sigma_g^+\ (v'=1) \leftarrow X^2\Sigma_g^+\ (v''=0)$	1.153	0.851–1.500
$a^3\Pi_u\ (v'=1) \leftarrow X^2\Sigma_g^+\ (v''=0)$	1.111	0.815–1.453

[a] Values are taken from Ref. [26].

[b] Calculated for acceleration through 1000 V.

To obtain a frequency-resolved Raman spectrum, we can integrate the signal intensity in the high energy region and normalize to the total electron signal. Fig. 3 shows the signal intensity as a function of Raman frequency at two laser powers, with the dashed line corresponding to high laser power and the solid line corresponding to low laser power. These spectra are superimposed on the *Q*-branch rotational structure expected for this transition, using the spectroscopic constants given by Rehfuss et al. [20] and assuming a rotational temperature of 95 ± 5 K, which is consistent with rotational temperatures measured previously on our apparatus under similar conditions [16]. The *Q*(0) transition occurs at a Raman shift of 1757.8 ± 0.1 cm^{-1} and higher *Q*-branch transitions occur further to the red.

Previous work in our laboratory [16] and elsewhere [27,28] has shown that both saturation and AC Stark broadening can contribute to linewidths in stimulated Raman spectra. Indeed, the higher power spectrum in Fig. 3 is nearly Gaussian, showing no hint of underlying rotational structure. The lower power spectrum is clearly asymmetric, and the individual rotational transitions making up the band are partially resolved. Even at the lower power, at which only 0.5% of the ions are being excited vibrationally, the linewidths of the individual rotational transitions are broader than the convolution of the pump and Stokes linewidths ($\sim 0.1\ \text{cm}^{-1}$). However, further reduction of the laser power leads to unacceptably low signal levels. The spectrum in Fig. 3 nonetheless illustrates that we can obtain at least partial rotational resolution of a *Q*-branch using this technique.

Signal levels in this experiment are comparable to our previous SRP study of C_2^-, in which vibrational excitation was detected by R2PD through the $B\,^2\Sigma_u^+$ excited state [16]. Because the R2PD transition was rotationally resolved, we could only detect SRP excitation of a single rotational level of C_2^- at each probe wavelength. The SRP-PES experiment allows us to measure the entire *Q*-branch at a single probe wavelength. Also, as mentioned above, SRP-PES does not require a bound intermediate state, so it should be applicable to a wider range of anions.

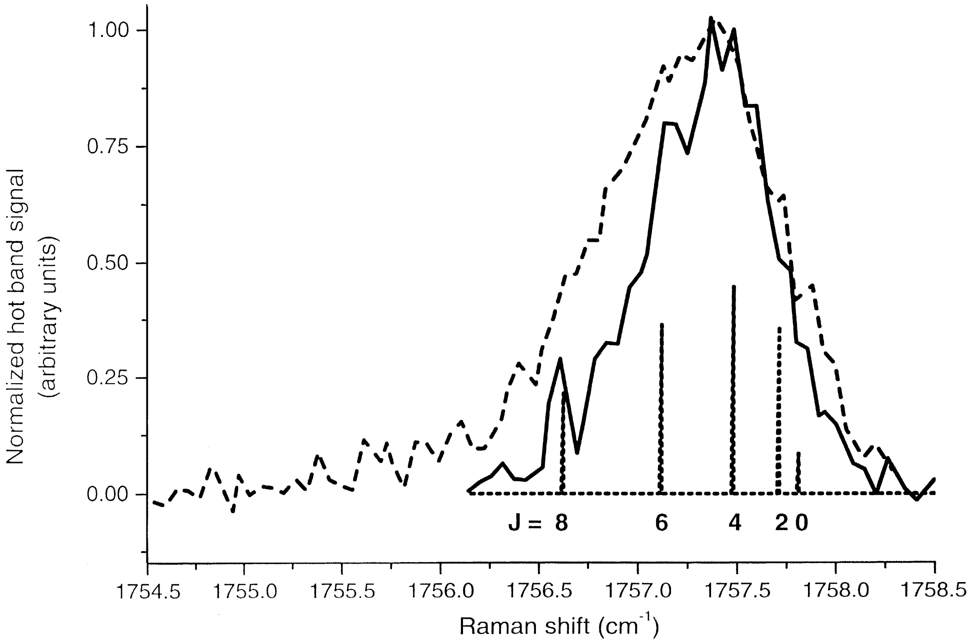

Fig. 3. Vibrational spectrum of the *Q*-branch of C_2^- in its ground $X\,^2\Sigma_g^+$ state. The ordinate is the integrated signal in the hot-band region of the photoelectron spectrum, normalized to the total electron signal and to the same maximum for both data sets. Dashed line: experimental data at high laser power (2 J cm^{-2} pump, 1 J cm^{-2} Stokes), 4500 shots/point; solid line: experimental data at low laser power (0.2 J cm^{-2} pump, 0.1 J cm^{-2} Stokes), 2000 shots/point; dotted trace: rotational stick spectrum assuming a Boltzmann distribution at 95 K.

4. Conclusion

We have demonstrated that stimulated Raman pumping can be combined with anion photoelectron spectroscopy in order to study the (ro-)vibrational spectroscopy of anions. For our test system, C_2^-, we have transferred up to 6% of the population of a given rotational level of the ground vibrational state to the vibrationally excited state. By monitoring the population transfer as a function of Raman shift, we have determined the vibrational transition frequency to be 1757.8 ± 0.1 cm^{-1}, in agreement with previous spectroscopic measurements, and we were able to resolve some rotational structure in the *Q*-branch.

The combination of mass-selectivity, high spectral resolution, and high detection efficiency, along with minimal requirements for the anions being studied, should make this new technique widely applicable. For some species we expect that vibrational excitation of the anion will allow us to see quite different areas of the neutral potential energy surface; one interesting class of candidates are the negative ion analogues of neutral bimolecular reaction transition states [29]. Experiments on these species will be carried out in the near future.

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