Air-Laser-Based Standoff Coherent Raman Spectrometer

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Abstract:

Among currently available optical spectroscopic methods, Raman spectroscopy has versatile application to investigation of dynamical processes of molecules leading to chemical changes in the gas and liquid phases. However, it is still a challenge to realize an ideal standoff coherent Raman spectrometer with which both high temporal resolution and high frequency resolution can be achieved, so that one can remotely probe chemical species in real time with high temporal resolution while monitoring the populations in their respective rovibronic levels in the frequency domain with sufficiently high spectral resolution. In the present study, we construct an air-laser-based Raman spectrometer, in which near-infrared femtosecond (fs) laser pulses at 800 nm and cavity-free picosecond N$_2^+$ air laser pulses at 391 nm generated by the filamentation induced by the fs laser pulses are simultaneously used, enabling us to generate a hybrid ps/fs laser source at a desired standoff position for standoff surveillance of chemical and biochemical species. With this prototype Raman spectrometer, we demonstrate that the temporal evolution of the electronic, vibrational and rotational states of N$_2^+$ and the coupling processes of the rovibrational wave-packet of N$_2$ molecules can be probed.

Keywords: Air lasing; nitrogen molecules; femtosecond laser; filamentation; Raman Spectroscopy.
1. Introduction

Spectrometers have been one of the most indispensable analytical tools to investigate frequency-dependent light-matter interactions that lie at the heart of a vast number of fundamental researches in astronomy, physics, chemistry and biology. This has led to the development of spectrometers with a variety of specifications such as the operation wavelengths, time-and-frequency resolutions, and size required in a variety of applications [1-4]. Chemical changes of molecules involve a variety of dynamical processes accompanied by the excitation of molecular rotations and vibrations, which can be probed by Raman-scattering based spectroscopic techniques with atomic spatial and femtosecond temporal resolution [5].

In the past few decades, a variety of approaches of vibrational Raman detections of chemical species have been developed to achieve high temporal resolution and high frequency resolution such as femtosecond stimulated Raman scattering (FSRS) [6, 7] and hybrid femtosecond/picosecond coherent anti-Stokes Raman scattering (fs/ps CARS) technique [8-11]. These vibrational Raman spectroscopic techniques provide direct insight into the vibrational level structures of molecules with high frequency resolution through a basic four-wave mixing process that is governed by the third-order nonlinear susceptibility \( \chi^3(\omega) \) [11, 12]. Therefore, the intensity of the resultant coherent Raman signal can be described as \( I(\omega) \propto \left| \left[ \chi^3(\omega) [E_S(\omega) \star E_p(\omega)] \right] \otimes E_{pr}(\omega) \right|^2 \), where \( \star \) and \( \otimes \) represent respectively the cross-correlation operator and the convolution operator, and \( E_p(\omega), E_S(\omega) \) and \( E_{pr}(\omega) \) represent respectively the electric fields of the three waves serving as the pump, Stokes and probe pulses to generate the fourth coherent vibrational Raman signals [10]. Therefore, a Raman spectroscopic measurement system by which we can achieve both the high temporal resolution and the high frequency resolution are in most cases large.
in size and expensive. In addition, it is not easy to use such an apparatus for the Raman detections at a standoff position because of the difficulty in spatiotemporal overlapping of the multiple laser systems with different wavelengths. On the other hand, it has been reported that air lasing with a few ps pulse duration and sub-10 cm\(^{-1}\) frequency resolution can be achieved remotely in the cavity-free scheme [13-20] and can be used as a light source in spectroscopic measurements inducing those in coherent Raman spectroscopy [21-24] as well as in distinguishing carbon isotopes of CO\(_2\) [25]. For remote sensing applications, we can optimize the energy of the air lasing and control the position in atmosphere where it is created in a manner that we reported before [26-28].

In the present study, we develop a standoff air-laser-based Raman spectrometer in which the intense fs near-IR pulsed laser and the ps 391 nm N\(_2^+\) laser created by the filamentation of the fs laser are used in combination, and demonstrate the capability of the spectrometer for probing in real time a coherent rovibrational wave packet of molecules and molecular ions in the air by the coherent Raman scattering processes including resonant and non-resonant coherent Stokes Raman scattering (CSRS) and anti-Stokes Raman scattering (CARS). In this spectroscopic scheme, the ps-pulsed N\(_2^+\) laser acts as a Raman pump to interact with a coherent rovibrational wave-packet of molecules and molecular ions created in the air by the fs pulsed laser at a desired standoff distance by varying the focal position, that is, the interaction position. By varying the temporal delay between the ps pump and fs activation laser pulses, the temporal evolution of the rovibrational wave packet of molecules and molecular ions are probed in real time. To the best of our knowledge, this is the first demonstration of an air-laser-based standoff Raman spectrometer with sufficiently high temporal and frequency resolutions. Because this characteristic and advantageous performance of the
air-laser-based coherent Raman technique can be realized by the nonlinear propagation
of intense NIR femtosecond laser pulses in the air, the unique spectrometer device is
promising to achieve remote sensing of chemicals and pollutants in the air, and thus,
has a variety of potential applications not only in fundamental molecular science but
also in environmental science.

2. Basic Principle and Methods

2.1 Principle and design of the standoff air-laser Raman spectrometer

The standoff Raman spectrometer is composed of the hybrid air-laser-based fs/ps
pulsed lasers, generated at a desired free-space position for the standoff detection of
chemical species. The roles of the hybrid laser pulses in the Raman spectrometer are
schematically shown in Fig. 1a. The broadband fs laser pulse whose bandwidth covers
the frequencies, \( \omega_1 \) and \( \omega_2 \), which initiates rotational and vibrational coherences in the
electronic ground state of molecular species of interest, thereafter called “a fs activation
pulse”. The rotational and vibrational wave packets of the system is probed after a time
delay \( \Delta t \) by the narrowband ps air-laser pulse, having the central frequency of \( \omega_3 \), that
drives the Raman transitions by the CSRS/CARS processes, thereafter called “a ps
pump pulse”. In our case, the fs laser pulse covers a broad spectral range of 710–840
nm with a pulse duration of \( \sim 60 \) fs, which is slightly chirped during the propagation in
the air, and the ps pump pulse has the narrow bandwidth of \( \sim 5 \) cm\(^{-1} \) and the pulse
duration of \( \sim 1.2 \) ps. The narrow bandwidth of the pump laser guarantees the high
spectral resolution of the standoff Raman spectrometer. The layout of the spectrometer
is schematically shown in Fig. 1b. The zero delay is defined as the timing when the
activation pulse is temporally overlapped with the ps pump pulse, and the positive delay
means that the activation pulse arrives the interaction zone before the ps pump pulse.
2.2 Methods

The air-laser Raman spectrometer was constructed based on a commercial Ti:sapphire laser system (Spectra Physics, Spitfire ACE) that produces intense ultrashort near-IR laser pulses (800 nm, 50 fs, 7.8 mJ/pulse, 200 Hz). The output of the laser system was...
split into two beams by a 9:1 beam splitter. The stronger beam (6.9 mJ/pulse) was focused by a lens (L1) (f = 400 mm) into a chamber filled with air at 20 mbar to generate population-inverted N$_2^+$. The weaker beam was converted into second-order harmonic pulses (400 nm, 500 nJ/pulse) by a 200-μm $\beta$-barium borate (BBO) crystal. The generated UV pulses acted as seed light to be amplified in the chamber, producing N$_2^+$ lasing at 391 nm. After passing through the chamber, the forwardly-propagating pulses were first collimated by a lens (L2) (f = 400 mm), and then, separated by a dichroic mirror (DM1) with a high reflectivity at 800 nm and a high transmittance in the ultraviolet-visible wavelength range. The generated N$_2^+$ laser (391 nm) having a narrow bandwidth of ~5 cm$^{-1}$ and a pulse duration of ~1.2 ps (see Fig. 2b) was isolated from the seed light (400 nm) by a band-pass filter (F1) with the transmission center wavelength of 390 nm and the bandwidth of 10 nm. The near-IR laser pulses (800 nm, 4.5 mJ/pulse), slightly chirped by the filamentation process and the propagation through the chamber so that the pulse duration is stretched to ~60 fs and the spectral range is broadened to 710–840 nm (see Fig. 2b), were reflected by DM1 and were purified by a long-pass (> 532 nm) filter (F2), and then, combined collinearly with the 391 nm laser pulses using another polished dichroic mirror (DM2) with a high reflectivity at 800 nm and a high transmission in the ultraviolet-visible wavelength region. The delay time between the 800 nm laser pulse and the 391 nm laser pulse was varied using a delay line (Thorlabs MT1-Z8) inserted in the beam path for the 800 nm laser pulses, which provides a minimum time delay step of 0.33 fs between the 800 nm activation laser pulse and the 391 nm Raman pump pulse. However, the time delay step was set to be 300 fs in the present study in order to record the Raman signals in the wide temporal range of 45 ps.
The spectrum of the 391 nm laser pulses is shown in Fig. 1b, which was measured after removing the D4 damper and inserting an attenuator before the spectrometer (Shamrock 303i, Andor). The spectrum of the 800 nm laser pulses is also shown in Fig. 1b, which was measured by dispersing the light of the 800 nm laser pulses scattered at a paper by a fiber spectrometer (HR4000, Ocean Optics). The pulse width of the 391 nm laser pulses was determined to be ~1.2 ps by the cross-correlation trace shown in the inset of Fig. 1b, which was recorded as the intensity variation of the sum-frequency pulses generated at a BBO crystal (500-μm thickness) by the 391 nm laser pulses and the 800 nm laser pulses attenuated to 300 μJ/pulse as a function of the delay between the two pulses. The zero delay is defined as the timing when the 800 nm pulse is temporally overlapped with the 391 nm laser pulse and the positive delay means that the 800 nm pulse arrives at the interaction point before the 391 nm laser pulse.

The 391 nm laser pulses, serving as the ps pump laser pulses, and the 800 nm laser pulses, serving as the fs activation laser pulses, were focused respectively by the L3 (\( f = 1 \) m) and L4 (\( f = 1 \) m) lenses. After passing through the focus, the laser beam was collimated by a lens (L5) (\( f = 750 \) mm) and the 800 nm component of the laser beam was reflected by a dichroic mirror (DM3). After passing through DM3, the laser beam was split into two by a 1:1 beam splitter (BM) (250–450 nm) and the laser beam passing through BM was dispersed by two prisms so that the supercontinuum and coherent Raman scattering light generated at the focus as well as the 391 nm laser beam were spatially separated, and finally, the supercontinuum in the visible range was blocked by a damper (D3). In addition, a metal strip damper (D4) was placed in the beam path, by which only the 391 nm laser beam was blocked, and the CSRS/CARS signals on the right and left spectral sides of the 391 nm laser, which were not blocked by D4, was reflected backward by an aluminum mirror (AM) and was focused by a lens (L6) (\( f = 6 \) m...
cm) into a spectrometer (Shamrock 303i, Andor) equipped with an ICCD (iStar, Andor). The slit width of the spectrometer was set to be at 200 μm, and the gate delay and gate width of the ICCD were set to be at −5 ns and 100 ns, respectively.

3. Results and Discussion

3.1 Air-laser Raman spectra

Figures 2 (a)-(c) show the spectra of air constituents measured with the fs activation laser-only (black dash line), the ps pump-only (blue dashed-dotted line), and the fs activation and ps pump (red solid line) at the delay time of Δt = 0 ps, 1.3 ps and 15 ps. The data were accumulated over 5000 laser shots to achieve a high signal-to-noise ratio as well as to reduce the influence induced by the shot-by-shot fluctuations in the activation laser parameters. It can be clearly seen in Figs. 2(a)-(c) that, only when both the activation and pump laser pulses are employed, several sharp peaks and broad bands at both red and blue sides of the 391 nm pump laser are generated, indicating that the ps pump laser at 391 nm laser pulse generates the coherent Raman scattering processes originating from the coherent media prepared by the fs activation laser pulse. It should be noted that the pump laser spectrum (blue lines) at 391 nm is strongly suppressed by D4, so that the relative spectral intensities of the P and R branches become different from those shown in Fig. 1b. The sharp peaks can be assigned to the coherent vibrational Raman lines of the Q-branch transitions of O2 at 1556 (11) cm\(^{-1}\) (CARS) and −1556 (7) cm\(^{-1}\) (CSRS) and those of N2 at 2330 (13) cm\(^{-1}\) (CARS) and −2330 (4) cm\(^{-1}\) (CSRS), where the numbers in the parentheses are the uncertainties in the measurements. The maximum conversion efficiencies from the air laser intensity to the vibrational Raman signals is estimated to be ~ 10\(^{-5}\) under the current experimental conditions.
In addition, the peak appearing at 427.8 nm, equivalently at the Raman shift of 
\(-2175 \pm 3\) cm\(^{-1}\), corresponds to the transition between the \(B^2Σ_u^+ (v' = 0)\) and \(X^2Σ_g^+ (v'' = 1)\) 
states of \(N_2^+\) and is assigned to the P-branch of the resonant vibrational Raman 
scattering (RVRS) of \(N_2^+\) because the 391 nm pump laser is resonant with the transition 
between the electronic states of \(B^2Σ_u^+ (v' = 0)\) and \(X^2Σ_g^+ (v'' = 0)\) states of \(N_2^+\), enhancing 
the Stokes Raman scattering. The small peaks at the blue side of the 427.8 nm RVRS 
peak, shown in the inset of Fig. 2 (b), are originated from the vibrational Raman 
scattering of the R-branch of the \(B^2Σ_u^+ (v' = 0)\) and \(X^2Σ_g^+ (v'' = 0)\) transition [29]. The 
bandwidth at full-width at half-maximum of the RVRS of \(N_2^+\) is 8 cm\(^{-1}\), which is 
slightly narrower than that (\(~12\) cm\(^{-1}\) of the CARS and CSRS signals of \(N_2\) and \(O_2\) due 
to the existence of the resonantly coupled upper levels. The double resonance also leads 
to more significant vibrational Raman scattering for the R-branch pump laser in the 
RVRS of \(N_2^+\) than in the CARS and CSRS of \(N_2\) and \(O_2\).
Fig. 2. Comprehensive air-laser Raman spectra. Raman spectra measured in the spectral range between $-2500$ and $2500$ cm$^{-1}$ recorded by the fs activation laser-only (black dash line), the ps pump laser-only (blue dashed-dotted line), and the fs activation laser and ps pump laser (red solid line) at the delay times of (a) 0 ps, (b) 1.3 ps and (c) 15 ps. The left-side inset in (c) indicates the spectral assignment of the sequential rotational CSRS at the head of the S-branch band of N$_2$ measured at the delay of $\Delta t = 6.3$ ps for the first (black solid), second (blue dash) and third (pink dash dot) orders of the S-branch rotational Raman signals of N$_2$. 
The broad bands (red solid line) shown in Fig. 2(a)-(c) are ascribed to both the sequential rotational Raman excited by the 391 nm pump pulse in a cascading manner [22] and the non-resonant CSRS and CARS (thereafter called non-resonant CRS) processes of the air molecules, whose intensities vary with the delay time in the full spectral range from $-2500$ cm$^{-1}$ to $2500$ cm$^{-1}$. The sequential rotational Raman scattering [22] can be seen more clearly as the peaks appearing on the top of the non-resonant continuum in the region of 0-1000 cm$^{-1}$. The left-side inset in Fig. 2(c) indicates that the significant sequential rotational CSRS signals at the head of the S-branch band of N$_2$ can be assigned to the first, second, and third orders of the rotational Raman signals of the S-branch ($J \rightarrow J-2$) of N$_2$, indicating that the sequential coherent rotational Raman signals mainly originate from N$_2$ molecules. In the non-resonant Raman scattering, many rotational and rovibrational levels coherently prepared by the fs activation pulse are involved. (See Discussion). As shown in Fig. 2(a), i.e., the spectrum measured at the delay of $\Delta t = 0$, where the activation laser overlaps with the peak of the 391 nm laser pulse, the non-resonant CARS are significantly enhanced, and sequential rotational Raman spectra (see the inset of Fig. 2(a)) can reach $-2500$ cm$^{-1}$. At the delay of $\Delta t = 15$ ps (Fig. 2(c)), the activation laser pulse arrives at the interaction region much earlier and does not overlap temporally with the ps pump pulse, non-resonant CRS could not occur [11]. Therefore, the broadband Raman signals are only attributed to the sequential rotational Raman process. The typical sequential rotational Raman spectrum in the range of $-900$ to $-550$ cm$^{-1}$ is shown in the right-side inset of Fig. 2(c), exhibiting rotational Raman peaks in the wide energy range originating from the cascading rotational excitations [22].
Fig. 3. Time-dependent Raman processes. (a) The delay time dependences of the non-resonant CRS (blue dotted line) of N$_2$, the CSRS (red dash line) of N$_2$, the CARS (pink dashed-dotted line) of N$_2$, and the RVRS (black line) of N$_2^+$. (b)-(e) The energy-level diagrams of the “non-resonant” CRS of N$_2$ (b), the CSRS (c) and CARS (d) of N$_2$, and the RVRS of N$_2^+$ (e). The inset in (a) shows the CARS spectra of N$_2$ in the range of 2200-2430 cm$^{-1}$ measured at the delay between the activation and Raman pump of $\Delta t = 6.3$ ps (blue solid line) and $\Delta t = 7.6$ ps (red dot line).

3.2 Time-dependent Raman processes

We measured, as shown in Fig. 3, the intensities of these three kinds of Raman processes, i.e., the non-resonant CRS in the range of 417-420 nm, corresponding to the Raman shit range between $-1567$ and $-1738$ cm$^{-1}$ (blue dash line), the vibrational...
CSRS/CARS of N\textsubscript{2} at \pm 2330 cm\textsuperscript{-1} (red dotted line/pink dash dotted line) and the RVRS of N\textsubscript{2}\textsuperscript{+} at –2175 cm\textsuperscript{-1} (black dotted line), as a function of the delay time. It can be seen in Fig. 3 that the temporal variation of the intensities of these three different kinds of Raman process are significantly different from each other. The time-dependence of the intensity of the non-resonant CRS is close to the temporal pulse shape of the 391 nm laser (see Method). That is, the maximum appears at \(\Delta t = 0\), where the activation laser temporally overlaps with the peak of the ps pump laser pulse. The slight difference between the non-resonant plot and the temporal profile of the 391 nm Raman pump laser can be ascribed to the delayed Kerr response effect in air molecules originating from the rotational transitions induced by the 800 nm activation laser front, which may affect the non-resonant Raman signals produced by the interaction with the rear part of the activation laser. Differently from the non-resonant CRS, the signal of the CSRS/CARS of N\textsubscript{2} takes the maximum intensity at \(\Delta t = 0.6\) ps, and the decay of the CSRS/CARS of N\textsubscript{2} is much slower than that of the non-resonant CRS. The decay of the RVRS signals of N\textsubscript{2}\textsuperscript{+} is the slowest and the signal of the RVRS signals of N\textsubscript{2}\textsuperscript{+} takes a maximum at the delay of 1.3 ps, which is latest among these three different Raman processes.

In order to understand the mechanisms of the generations of these Raman signals recorded by our spectrometer, i.e., the broadband non-resonant CRS, the vibrational CSRS/CARS of N\textsubscript{2} and the RVRS of N\textsubscript{2}\textsuperscript{+}, we show the schematic energy-level diagrams in Figs. 3 (b)-(e). The intensity of the coherent Raman signals is proportional to \(\left| P^{(3)} (\omega) \right|^2\), in which the \(P^{(3)} (\omega)\) represents the third-order polarization and can be described as \[11\]

\[
P^{(3)} (\omega) = P_{NR}^{(3)} (\omega) + P_R^{(3)} (\omega),
\]

(eq. 1)
where $P_{NR}^{(3)}(\omega)$ is the non-resonant component, which can be written as

$$P_{NR}^{(3)}(\omega) = \int_{0}^{+\infty} d\Omega \times \chi_{NR}^{(3)} \times E_{3}(\omega \pm \Omega) \times S_{12}(\Omega),$$  
(eq. 2)

where $\Omega$ denotes the frequency difference between the two electric-field amplitudes, $E_{1}(\omega)$ and $E_{2}(\omega)$, contributing to the Raman scattering process within the bandwidth of the broadband activation laser, $S_{12}(\Omega)$ denotes the convolution of the $E_{1}(\omega)$ and $E_{2}(\omega)$, which can be written as

$$S_{12}(\Omega) = \int_{0}^{+\infty} d\omega' \times E_{1}(\omega') E_{2}(\omega' - \Omega),$$  
(eq. 3)

$E_{3}(\omega)$ represents the electric field amplitude of the narrow-band ps pump laser, $\chi_{NR}^{(3)}$ represents the “non-resonant” third-order susceptibility, which is usually insensitive to the frequency and can be assumed to be constant [11]. Therefore, the non-resonant contribution induces a smooth broadband spectral profile inherited from the $S_{12}(\Omega)$ as shown in the Fig.2 (a) and (b), which may cover the spectral ranges of the vibrational and rotational transitions of the molecular species of interest in the present study. Because the non-resonant CRS processes are insensitive to the transition frequencies, their transition schemes can be expressed using the virtual levels in the electronic ground state as expressed by the energy level diagram in Fig. 3(b) (virtual levels). The non-resonant CRS occurs only in the period during which the fs activation laser pulse and the ps pump laser pulses overlap temporally [9]. This is the reason why its delay curve follows the profile of the ps pump pulse in the time domain and takes the maximum value when the activation pulse temporally overlaps with the peak of the ps pump laser pulse.

In the resonant case, $P_{R}^{(3)}(\omega)$ becomes dominant and can be written as
\[ P_{R}^{(3)}(\omega) = \int_{0}^{+\infty} d\Omega \times \chi_{R}^{(3)}(\Omega) \times E_{3}(\omega \pm \Omega) \times S_{12}(\Omega), \]  
(eq. 4)

where \( \chi_{R}^{(3)} \) represents the resonant three-order susceptibility. The vibrational CSRS/CARS of N\(_2\) at \( \pm 2325 \text{ cm}^{-1} \) can be attributed to the singly resonant case [12], in which the two coherent real vibrational states of N\(_2\) that are populated by two photons whose frequency difference matches the separation of the two vibrational levels (see the energy level diagrams in Figs. 3(c) and (d)). Therefore, the \( \chi_{R}^{(3)} \) can be written a

\[ \chi_{R}^{(3)}[\omega = \omega_3 \pm (\omega_1 - \omega_2)] = \frac{a}{(\omega_1 - \omega_2 - \omega_v) + i\Gamma_v}, \]  
(eq. 5)

where \( \omega_1 \) and \( \omega_2 \) represent the frequencies of the two photons provided by the fs activation laser pulse, and the \( \omega_3 \) represents the frequency of the photon of the ps pump laser pulse. The coefficient \( a \) represents the strength of the single resonance which is independent of \( \omega_1 \) and \( \omega_2 \) because \( \omega_1 - \omega_2 \) is scanned over the Raman resonance, \( \Gamma_v \)

represents the half-width of the vibrational Raman peak profile, and \( \omega_v \) represents the vibrational frequency. It can be seen that the resonant susceptibility can be significantly enhanced when \( \omega_1 - \omega_2 = \omega_v \). Because the decay profiles of N\(_2\) CSRS/CARS are related to the dispersion of the wave packet of N\(_2\) originating from the anharmonicity of the molecular potential energy curve and the rotation-vibration coupling [30], the N\(_2\) CSRS/CARS can remain even after the activation laser pulse disappears. After \( \Delta t = 1.6 \) ps, the fs activation laser pulse and the ps pump laser pulse are temporally separated almost completely, the intensity of the CSRS/CARS of N\(_2\) decreases as \( \Delta t \) increases, as shown in the Fig. 3(a), which can be ascribed to the dispersion of the vibrational wave packet originating from the anharmonicity of the molecular potential energy surface and rotation-vibration coupling [30].
The maximum intensity of the CSRS/CARS of N$_2$ appears at the delay of $\Delta t \sim 0.6$ ps. This is because, at the delay of 0 ps, the front part of the ps pump laser pulse arrives at the interaction zone before the fs activation laser pulse and the CSRS/CARS process cannot be induced efficiently. Therefore, the optimized CSRS/CARS intensities in the N$_2^+$-laser-based coherent Raman spectroscopy can be obtained when $0 < \Delta t < 1.6$ ps.

Moreover, when the two pulses temporally overlap at $\Delta t = 0$ ps, the shading of the Q-branch head of the vibrational CSRS/CARS towards the higher frequency side develops significantly, and consequently, the Q-branching head cannot form the sharp peak profile at the rotational band origin.

Furthermore, it can be seen in Fig. 3(a) that oscillation structures with a period of ~2 ps appear in the decaying tails of the CSRS and CARS curves for the delay range of 0-10 ps. To explore the origin of these oscillation structures, we show in the inset of Fig. 3 the two CARS spectra of N$_2$ in the range of 2200-2430 cm$^{-1}$ measured respectively when the delays between the activation and Raman pump were at $\Delta t = 6.3$ ps (blue solid line) and $\Delta t = 7.6$ ps (red dot line), which correspond to the minimum and maximum intensities of the oscillation structures marked by the black dotted line in the Fig. 3(a). The inset of Fig. 3(a) clearly shows that the vibrational Q-branch transition of N$_2$ at ~2330 cm$^{-1}$ (marked by the black dashed line in the inset) is directly induced by the 391 nm pump laser. In addition, the second-order vibrational Q-branch transition of N$_2$ at the Raman shift range between ~2342 cm$^{-1}$ and ~2390 cm$^{-1}$ (marked by the pink dotted lines in the inset) are observed and the rotational S-branch Raman laser of N$_2$ induced by the 391 nm pump laser are observed in the Raman shift range between ~12 cm$^{-1}$ and ~60 cm$^{-1}$. This is confirmed by the comparison of the Raman shifts in the peaks in the inset of Fig. 3(a) with those shown in the left-side inset of Fig. 2(c). Therefore, the oscillation structures appearing in the CSRS and CARS signals...
shown in Fig. 3(a) can be ascribed to the intensity variation in the 391 nm pump laser modulated by the rotation of \( N_2 \) with a quarter period of ~2 ps, resulting in the energy transfer from the 391 nm pump laser to the sequential rotational Raman laser.

For the RVRS of \( N_2^+ \) at ~2172 cm\(^{-1} \), it can be seen from the energy diagram shown in Fig. 3(e) that, besides the two low-lying vibrational levels, the coherent vibrational Raman transition consists of a one-photon resonant electronic transition, which can be interpreted by the doubly resonant cases [12]. Therefore, the \( \chi^{(3)}_R \) can be written as

\[
\chi^{(3)}_R[\omega = \omega_3 - (\omega_1 - \omega_2)] = \frac{b}{[(\omega_1 - \omega_2 - \omega_v) + i\Gamma_v][(\omega_3 - \omega_1 + \omega_2 - \omega_v) + i\Gamma_e]},
\]

where \( b \) represents the strength of the double resonance, \( \Gamma_v \) and \( \Gamma_e \) represents respectively the half-widths of the vibrational and electronic transition peak profiles and \( \omega_v \) and \( \omega_e \) represent respectively the frequencies corresponding to the vibrational and electronic transitions.

After the multiphoton/tunnel ionization of \( N_2 \) by the fs activation laser, the coherence of the two vibrational states, i.e., the \( X^2\Sigma_g^+(\nu''=1) \) and \( X^2\Sigma_g^+(\nu''=0) \) states of \( N_2^+ \) is prepared. In addition, the rear-part of the spectrally broadened fs activation pulse can also contribute to the creation of the coherence of the two vibrational levels. The ps pump laser which is resonant with the electronic transition between the \( B^2\Sigma_u^+(\nu'=0) \) and \( X^2\Sigma_g^+(\nu''=0) \) states induces the RVRS process. The decay time of the RVRS of \( N_2^+ \) is much longer than that of CSRS/CARS of \( N_2 \), which may be attributed to the smaller dispersion in the vibrational wave packet of \( N_2^+ \).

In addition, the maximum of the RVRS appears at \( \Delta t = 1.3 \) ps, which is later than those in the non-resonant CRS and CSRS/CARS. This may be ascribed to the fact that
the ps pump laser is electronically resonant with the \( B^2\Sigma_u^+(\nu' = 0) - X^2\Sigma_g^+(\nu'' = 0) \) transition.

Because the dispersion of the vibrational wave packet originates from the anharmonicity of the molecular potential energy curve and rotation-vibration coupling [30], the decay of RVRS reveals the temporal evolution of the electronic, vibrational and rotational states of \( \text{N}_2^+ \).

4. Conclusion

In summary, by introducing the Raman spectroscopic signatures of the atmospheric constituents, we have demonstrated that our spectrometer provides simultaneous standoff detections of the coherent resonant and non-resonant rotational and vibrational Raman processes of molecules with the high temporal resolution and the high frequency resolution. The key advantages of this technique originate from the ps pump laser generated by the filamentation created by the intense fs-pulsed laser in the atmosphere, producing the hybrid air-laser-based ps/fs laser pulses at a desired free-space position. We have conducted a proof-of-principle demonstration of our spectrometer by the observation of the temporal evolution of the rovibrational wave packet of \( \text{N}_2 \) as well as by the observation of the temporal evolution of the electronic, vibrational, and rotational wave packet of \( \text{N}_2^+ \). This air-laser-based coherent Raman technique with high frequency resolution and high temporal resolution can easily be implemented in standoff spectroscopy for remote sensing of chemicals and pollutants in the air. In conclusion, the concept of this standoff air-laser Raman spectrometer opens new opportunities for researchers to explore remote detection and surveillance of chemical and biochemical species with sufficiently high temporal and frequency resolutions.

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Author contributions

H. L. X. and K.Y. developed the concept and designed the experiment. Y. F., J. C. C., and H.L.X. performed the experiments. Y. F., J. C. C., K. Y. and H. L. X. analyzed the data. The manuscript was prepared by Y. F., K. Y., and H. L. X., and was discussed among all authors.

Data availability

The data that support the plots within this article and other findings of this study are available from the corresponding author(s) upon reasonable request.

Competing interests

The authors declare that there is no conflict of interest regarding the publication of this article.

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