

Infrared Upconversion for Astronomy

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Abstract

The field of infrared upconversion for astronomy is reviewed. The basic theory of upconversion is presented, along with a brief historical summary of upconversion techniques. Several investigators have employed upconverters in astronomical studies, but have met with only modest success. Upconversion will become a useful detection method for astronomy only if substantial but perhaps foreseeable improvements can be realized.

Introduction

A novel solution to the problem of infrared detection is afforded by the process of upconversion. The upconversion process is shown schematically in Figure 1. Infrared radiation of frequency

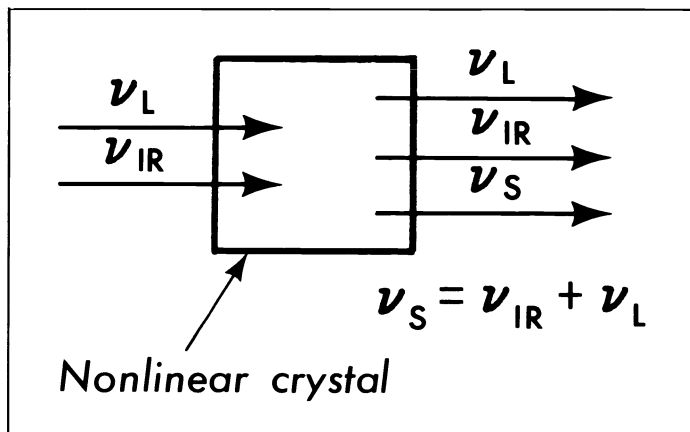


Figure 1. Schematic description of the upconversion process. Infrared radiation of frequency ν_{IR} is mixed with an intense laser beam of frequency ν_L in a nonlinear crystal, producing a signal at the sum frequency ν_S .

ν_{IR} is mixed with an intense visible or near-infrared laser beam of frequency ν_L in a nonlinear crystal. The nonlinearity causes a signal to be generated at the sum frequency, ν_S , which is in the visible region; thus the infrared signal is converted to the visible, where sensitive, low noise detectors are readily available. The conversion efficiency of infrared photons to visible photons at the sum frequency can approach 100%.¹ Furthermore, the upconversion process is inherently noise free in the sense that energy conservation prohibits the generation of a response at the sum frequency in the absence of a signal at the infrared frequency.

A related use of the upconversion process is to convert images from the infrared spectral region to the visible. As illustrated in Figure 2, the upconversion process, in conserving photon momentum ($\hbar\vec{k}$), insures that a one-to-one correspondence exists between infrared directions of propagation and sum frequency di-

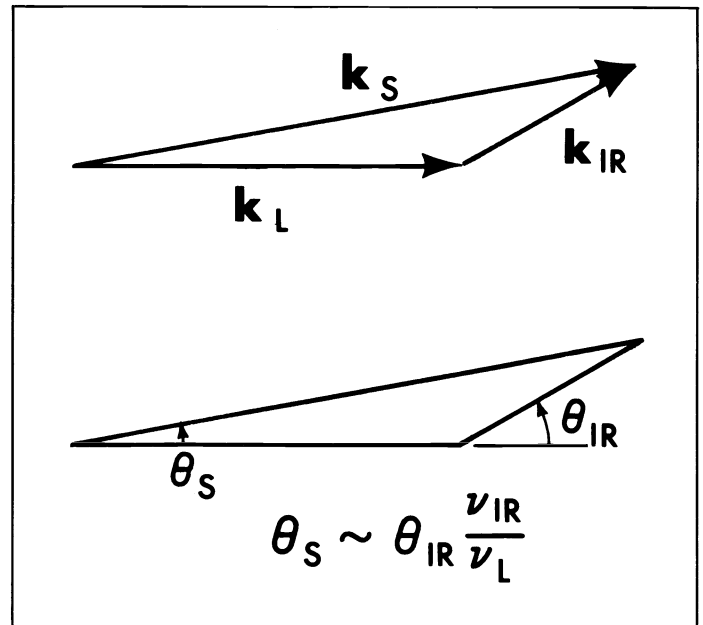


Figure 2. Imaging property of the upconversion process. Conservation of photon momentum ($\hbar\vec{k}$) requires that the sum frequency photon be emitted in a unique direction.

rections of propagation. In fact, to a good approximation, the angle of propagation of the sum frequency radiation is related to the angle of propagation of the infrared radiation by

$$\theta_S \approx \theta_{IR} \frac{\nu_{IR}}{\nu_L} \quad (1)$$

where θ_S and θ_{IR} are defined in Figure 2. Thus, if the optical system which collects the infrared radiation is designed so as to map each point in the field of view into a plane wave at the crystal with a direction of propagation θ_{IR} , Eq. (1) predicts that the sum frequency response will be a perfect image of the infrared field, demagnified by the factor ν_{IR}/ν_L .

This article will review the various instruments for astronomy which have been constructed using the upconversion process. Despite the potential of the technique, only modest results have been achieved to date. One serious problem has been that the quantum conversion efficiency has been quite low for upconverters employing continuous wave lasers. An additional problem is that many workers in the field have been limited by noise sources larger than expected. As a result, the technique has yielded only marginal results in terms of astronomical detection. However, since the problems to date do not appear to be ones of principle, it is hoped that upconversion may become a useful detection technique at some future time.

Upconversion Theory

Some of the theoretical aspects of the upconversion process will

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be considered in this section. Only those fundamentals needed to understand the description of various upconversion systems discussed later will be provided. The excellent treatments of Hulme² and of Midwinter and Zernike³ are recommended for those desiring additional information.

When transparent matter is subjected to intense electromagnetic radiation, the response of the matter (measured by the polarization, or dipole moment per unit volume) ceases to be linearly dependent on the incident field amplitude and displays nonlinear effects. The lowest order nonlinearity gives rise to the second order polarization, and it is this nonlinearity that is exploited in most upconverters. If \vec{E}_L and \vec{E}_{IR} are the electric field amplitudes associated with the laser beam and infrared field, respectively, the nonlinearity will induce a second order polarization of amplitude \vec{P} within the nonlinear crystal at the sum and difference frequencies, where \vec{P} is given by

$$P_i = 2 \sum_{j,k} d_{ijk} E_j^L E_k^{IR} \quad (2)$$

d_{ijk} is the nonlinear coefficient of the medium, and the indices i, j , and k refer to cartesian components. In practice, d_{ijk} can almost never be calculated, and is regarded as an empirical constant.

Not all optically transparent materials allow this lowest order nonlinearity to exist. Only materials which are not symmetric under inversion can give a second order polarization, and this restriction limits the class of crystals of interest in upconversion work. Materials with inversion symmetry are still of interest in nonlinear optics, however, as they can participate in higher order nonlinear interactions. Since these higher order interactions are generally less intense than the lowest order nonlinear interaction, they have only recently been exploited in experimental studies.

The time varying polarization \vec{P} within the nonlinear medium can radiate energy efficiently only if the various dipoles can act as a phased array, and this requires that the condition

$$\vec{k}_L + \vec{k}_{IR} = \vec{k}_S \quad (3)$$

between the propagation vectors of the three waves be satisfied, as well as the condition defining the sum frequency

$$\nu_L + \nu_{IR} = \nu_S \quad (4)$$

In general, these conditions are incompatible. For a birefringent crystal, however, the index of refraction is dependent upon the direction of the E vector, and thus for certain choices of polarization and propagation directions Eqs. (3) and (4) can be simultaneously satisfied, and under this condition the interaction is said to be phase-matched. When phase-matching is obtained by rotating the crystal so as to vary the direction of propagation within the crystal, the upconverter is said to be angle tuned. In some cases the refractive indices of the nonlinear crystal are sufficiently temperature dependent that the phase-matching condition can be met by accurately controlling the crystal temperature, which is referred to as temperature tuning. In practice, it is almost always the case that if the sum frequency generation process is phase-matched, the difference frequency process will be badly mismatched, and hence no appreciable power will be generated at the difference frequency.

Perhaps the most important parameter describing an upconversion system is the quantum efficiency, or the ratio of the number of sum frequency photons produced to the number of infrared photons entering the nonlinear crystal. Since Gaussian electrostatic units are the units most often used in nonlinear optics, this convention will be followed here. For the (unfortunately) usual case of small quantum efficiency, the quantum efficiency is given by

$$\eta = \frac{512 \pi^5 d_{eff}^2 I_L \ell^2}{n_{IR} n_L n_S \lambda_S \lambda_{IR} c} \left[\frac{\sin(\ell \Delta k / 2)}{\ell \Delta k / 2} \right]^2 \quad (5)$$

where Δk is the propagation vector mismatch

$$\Delta k = |\vec{k}_S - \vec{k}_L - \vec{k}_{IR}| \quad (6)$$

ℓ is the length of the nonlinear crystal, c is the velocity of light; n_{IR} , n_L , and n_S are the indices of refraction for the three waves; λ_{IR} and λ_S are the vacuum wavelengths of the sum and infrared fields, I_L is the laser power per unit area, and d_{eff} is the effective value of d_{ijk} obtained by carrying out the summation indicated in Eq. (2). For the case of perfect phase-matching the term in square brackets in Eq. (5) is equal to one. We note that the system quantum efficiency is proportional to d_{eff}^2 , to the laser power per unit area, and to the square of the length of the crystal. This last result follows from the phase-matching condition which allows the individual dipoles within the crystal to radiate coherently.

The infrared bandpass of an upconverter is limited to the extent that the term in square brackets in Eq. (5) falls to zero as Δk increases as a result of the infrared frequency being varied from its central value. The actual value of the bandpass will depend upon the details of the dispersion of the refractive indices for any particular crystal, but a good rule of thumb is that the infrared bandpass in cm^{-1} is numerically equal to the inverse of the length of the crystal in cm, and it is generally true that the bandpass is inversely proportional to the length of the nonlinear crystal.

For an imaging upconverter, the questions of angular resolution and field of view are also raised. While the phase-matching conditions place a serious constraint on the cone angle of radiation of any particular wavelength that can be efficiently upconverted, it has been found that the field of an imaging upconverter can be quite large in that different infrared wavelengths are upconverted at different angles within the field of view.⁴ While this may be an undesirable feature for some spectroscopic work, it should not present a problem in the imaging of thermal sources. Under certain conditions, the angular resolution of an upconverter will be limited only by diffraction. In particular, if a single transverse mode laser is used to illuminate an optically perfect crystal with faces flat to $\lambda/10$ at all relevant wavelengths, the configuration discussed earlier in which collimated infrared is upconverted to the visible will result in visible images whose sharpness is degraded only by the uncertainty in propagation angle due to the diffraction of the infrared beam. Thus, no information is lost in the upconversion process.

Historical Survey of Upconversion

In this section, the historical development of upconversion for detection of infrared radiation will be outlined. No attempt at completeness will be made; rather, only some of the most significant theoretical and experimental results will be presented. In the following section an account of all reported applications of upconversion to astronomy will be presented.

Nonlinear optics is almost as old as the laser itself. The first working laser was constructed by Maiman⁵ following a suggestion of Schawlow and Townes.⁶ By 1961, Franken et al⁷ had succeeded in observing the second harmonic of ruby laser light using crystal quartz as a nonlinear material. The necessity of phase-matching if high conversion efficiency were to be achieved was apparent, and in 1962 Giordmaine⁸ and Maker et al⁹ independently succeeded in utilizing birefringence to realize the phase-matching condition.

Armstrong et al¹⁰ considered the general case of sum frequency generation in addition to the degenerate case of second harmonic generation, and developed a general theory of these processes, treating the nonlinear material using quantum mechanical perturbation theory and using Maxwell's equations to describe the optical field. Furthermore, they suggested using the upconversion process as a method of detecting infrared radiation. The first experimental studies of upconversion were those of Johnson and Duardo¹¹ and Midwinter and Warner.¹² Midwinter

and Warner upconverted $1.7\text{ }\mu\text{m}$ infrared radiation in a 6 cm^{-1} bandpass to the visible by mixing with a pulsed ruby laser beam in a temperature tuned lithium niobate crystal. They achieved a maximum conversion efficiency of 1% at their peak power density of 1 MW/cm^2 . The noise performance of their upconverter was worse than theoretical due to an unidentified source of noise at the sum frequency. The source of noise was assumed to be upconverted infrared radiation because the noise was polarized in the same sense as the sum frequency radiation and appeared to be phasematched. They speculated that the source of infrared noise was either dust particles heated by the laser beam, fluorescence of one of their optical components, or a higher order nonlinear process, but they could not isolate the actual source.

Motivated by this observation of an unexpected noise source, Smith and Townes¹³ investigated several possible higher order processes which could produce noise, the most important being the parametric process in which a laser photon is annihilated, creating an infrared photon and a difference frequency photon, with the infrared photon being subsequently upconverted by the usual phasematched upconversion process. Using semiclassical arguments, Smith and Townes estimated that while this process could be an appreciable source of noise, it could not have produced as much noise as that measured by Midwinter and Warner. They also concluded that these higher order noise sources could be rendered negligibly small by a suitable choice of system parameters and hence upconversion was a potentially attractive method of high sensitivity infrared detection. These results were corroborated by Tang,¹⁴ who repeated these calculations using a fully quantized field approach.

Imaging upconversion was first reported by Midwinter¹⁵ who achieved 50 lines of resolution across his field of view. Theoretical discussions of imaging upconversion were given by Midwinter,¹⁶ Warner,¹⁷ and Firester.¹⁸ Warner pointed out that the angular field of view for upconversion of monochromatic infrared can be made quite large for certain geometries in which the three waves are not colinearly propagating. This suggested that a scene actively illuminated by a $10.6\text{ }\mu\text{m}$ CO_2 laser could be usefully studied by imaging upconversion. Experimental investigations of upconversion imaging of actively illuminated scenes have been carried out by Lucy¹⁹ and Tseng.²⁰ Firester¹⁸ clarified the role of laser beam divergence in limiting the angular resolution of an imaging upconverter. In particular, a single transverse mode laser beam need not have plane wavefronts in order for the upconverter to achieve maximum resolution, in disagreement with the prevailing view at that time. A curvature to the laser wavefronts will simply displace the focus of the upconverted image.

Falk and Yarborough²¹ first succeeded in detecting room temperature thermal radiation with their Nd:YAG laser pumped proustite upconverter. Gurski¹ succeeded in obtaining almost 100% conversion of $3.39\text{ }\mu\text{m}$ radiation into visible radiation with his ruby laser ($0.6943\text{ }\mu\text{m}$) pumped lithium iodate upconverter.

A potentially great improvement in upconverter sensitivity is possible using the technique developed by Harris and his co-workers at Stanford University, in which the third order nonlinearity of a metal vapor is utilized.²² As atomic transitions tend to be quite narrow, it is possible to work very close to resonance, with a corresponding increase in the efficiency of the nonlinear coupling. Bloom et al²² reported the operation of such a device to convert $9.26\text{ }\mu\text{m}$ infrared radiation to the near ultraviolet at $0.3305\text{ }\mu\text{m}$, by mixing with $0.6856\text{ }\mu\text{m}$ optical parametric oscillator radiation (3 kw peak power) in a sodium cell. The nonallowed 3s-3d transition of sodium is pumped by the second harmonic of the optical parametric oscillator, giving a resonant enhancement to the conversion process. Despite the fact that no effort was made to phasematch the process, a photon conversion efficiency of 58% was reported. Such a device would have limited use in astronomy due to the relatively low duty cycle ($\sim 10^{-6}$) of their optical parametric oscillator.

Stappaerts et al²³ have constructed an imaging upconverter operating on similar principles. Their device converts $2.9\text{ }\mu\text{m}$

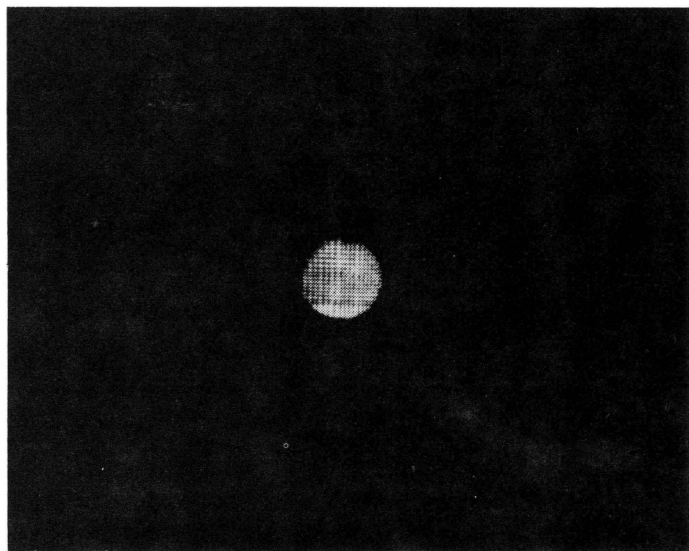


Figure 3. Upconverted image of a resolution test pattern by Stappaerts et al.²³ They estimate that the original photograph consists of at least 1000 resolvable spots.

radiation to $.455\text{ }\mu\text{m}$ with a quantum efficiency of 3%. Their final images contained 1000 resolution elements (see Figure 3), and again, the usefulness of the device for astronomical applications was limited by the requirement that their laser be a pulsed source.

Another new technique is that discussed by Bethune et al²⁴, in which sum frequency generation is induced via quadrupole transitions in sodium vapor. Whereas sum frequency generation is disallowed in the dipole approximation for isotropic media such as atomic vapors, this process is allowed for quadrupole transitions. Being a lower order nonlinear process than the third order allowed process of Bloom et al, it is found to be of comparable intensity. This process relies on a resonant enhancement to increase the magnitude of the nonlinear interaction, and thus requires the use of tunable laser sources. This technique has not yet been exploited for infrared detection.

Astronomical Instruments

The first reported use of an upconverter for astronomical work was that of Gurski et al.²⁵ This system used a pulsed Nd:YAG laser pumped lithium iodate upconverter, yielding a peak quantum conversion efficiency of 10^{-3} . Phasematching was achieved by angle tuning the 5 cm long crystal; extremely fortuitous dispersion of lithium iodate allowed the extremely wide bandpass of $1.8\text{ }\mu\text{m}$ extending from $3.2\text{ }\mu\text{m}$ to $5.0\text{ }\mu\text{m}$. Gurski et al found it convenient to pulse their laser at a 0.5 Hz repetition rate, yielding a duty cycle of 10^{-3} for the 2.0 ms pulse duration. The system was capable of operating at a 6% duty cycle, however.

With this system, Gurski et al were able to detect the near infrared flux from the Moon, Venus, α Ori, and α Tau at a 2σ level in 100 seconds of real time for the first two objects and in 200 seconds for the second two objects. Taking their duty cycle into account, the actual data-taking took place in 0.1 and 0.2 sec, respectively. An excess noise source was found which they attributed to an absorption band in their crystal. However, sky and telescope noise were the predominant sources of noise. Taking photomultiplier quantum efficiency and the imperfect transmission of their optics into account, Gurski et al estimate losses of a factor of 100, yielding a peak system quantum efficiency of 10^{-5} , and a time averaged system quantum efficiency of 10^{-8} .

An infrared upconverter with an inherently narrow bandpass for spectroscopic applications has been described by Smith.²⁶ His system utilized the nonlinearity of a 5 cm long lithium niobate crystal to mix a temperature tuneable ($2.8\text{ }\mu\text{m}$ to $4.2\text{ }\mu\text{m}$)

infrared signal of 1 cm^{-1} bandpass with a one watt, cw, argon ion laser pump ($0.5145 \mu\text{m}$), to yield a sum frequency at about $.450 \mu\text{m}$. Smith's upconversion quantum efficiency was 10^{-4} , although he achieved 3×10^{-3} under conditions not optimum for coupling to a telescope. His losses of about 1000 yielded a system quantum efficiency of 10^{-7} . His measured NEP was $10^{-13} \text{ watts/Hz}^{1/2}$.

With this apparatus, Smith was able to detect the Moon, α Ori, and α Boo. A spectrum of α Ori is shown in Figure 4. Al-

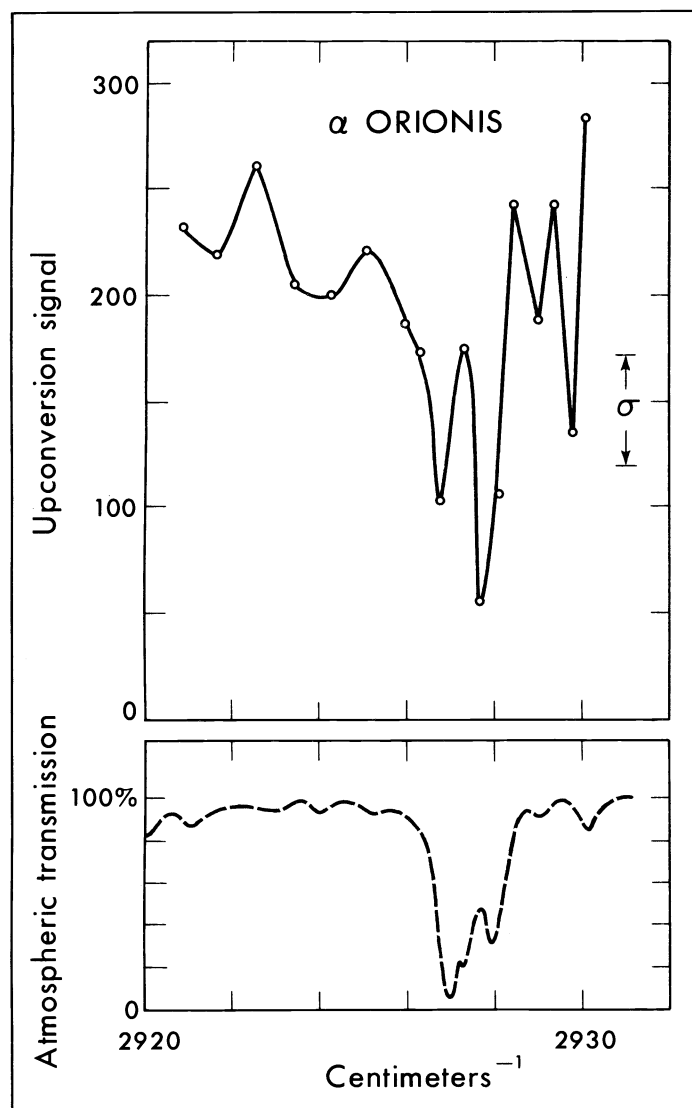


Figure 4. α Orionis spectrum, taken in one-half hour on the 120" telescope at Lick Observatory by Smith.²⁶ The features are all telluric, as can be seen by comparison with the lower curve, taken at a different, drier site.

though the feature detected is of telluric origin, and hence not of particular astronomical interest, this observation indicates that upconverters are nearly capable of providing useful spectroscopic information regarding astronomical sources.

Smith also was troubled by an unexpected source of noise in his system, and in fact this additional noise source was the primary limitation to his system NEP. Smith made a concerted effort to ascertain the cause of this noise contribution, and concluded that none of the usual explanations (crystal emissivity, radiation from his crystal oven, fluorescence of optical components) could contribute the measured amount. Smith and Townes²⁷ have developed a theory which could account for the unexpected noise sources encountered by so many of the workers in upconversion. In this theory thermal energy mixes

with the laser beam to produce upconverted photons. Vacuum fluctuations provide electromagnetic coupling between the crystalline ground state and infrared levels which allows the process to be coherent and phase matched. This process is more intense than upconversion of infrared radiated by the crystal itself.

Abbas et al²⁸ have reported the construction of a system similar to that of Smith, but employing a chopped infrared beam and the use of phase sensitive detection of the sum frequency radiation. This procedure minimizes the effects of drifts in their system parameters, and allows them to obtain a system NEP of $10^{-14} \text{ W/Hz}^{1/2}$. They have not yet used their upconverter for astronomical detection, but their published paper presents a discussion of the use of such a system for astronomical applications. A laboratory spectrogram of methane obtained with their upconverter is shown in Figure 5.

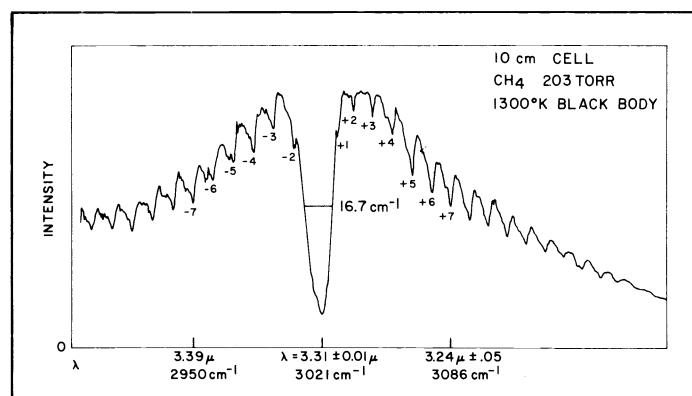


Figure 5. The absorption spectrum of methane measured with the upconverter of Abbas, et al,²⁸ showing the P, Q, and R branches. The upconverter spectral resolution was $\sim 2.7 \text{ cm}^{-1}$. 40 minutes of integration were required to take this spectrum.

Infrared imaging of astronomical sources by upconverting their $10 \mu\text{m}$ radiation has been reported by Boyd.²⁹ His system, shown in Figure 6, uses an 0.25 watt cw krypton ion laser beam at $0.7525 \mu\text{m}$ to pump a 1-cm-long proustite crystal. An infrared bandpass of 2 cm^{-1} is tunable from $9 \mu\text{m}$ to $11 \mu\text{m}$ by angle tuning the proustite crystal. The upconversion quantum efficien-

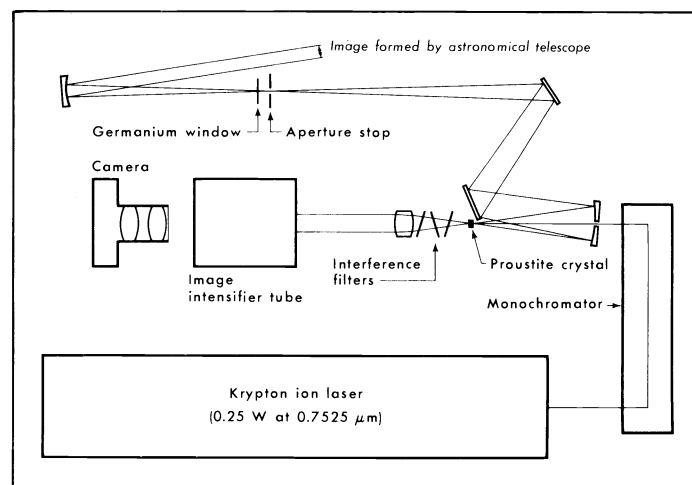


Figure 6. $10 \mu\text{m}$ imaging upconverter of Boyd.²⁹ The monochromator is used to eliminate background light from the laser discharge tube. Collimated infrared radiation is mixed with the laser beam in the proustite crystal. The interference filters pass the sum frequency while rejecting the laser frequency, providing a factor of 10^{18} discrimination between the two frequencies. The sum frequency image is amplified by the image intensifier tube and recorded photographically.

cy is 2×10^7 , and the system quantum efficiency is 1×10^9 . The angular resolution of the system is very nearly diffraction limited; laser induced heating of the proustite crystal distorts the sum frequency wavefronts so as to degrade system resolution to 75% of theoretical. Sum frequency pictures contain approximately 300 resolution elements.

As an astronomical device, the system is mounted at the focus of the 1.5 m McMath Solar Telescope of Kitt Peak National Observatory, yielding a field of view of 40 seconds of arc, with a resolution of 2.5 seconds of arc. Images were obtained of the Sun, Moon, Mercury, and the star VY Canis Majoris, in limiting exposure times of 2 sec, 2 min, 1 min, and 15 minutes, respectively. Results are shown in Figure 7. Comparisons of astronomical seeing at $10 \mu\text{m}$ and at visible wavelengths were also obtained.

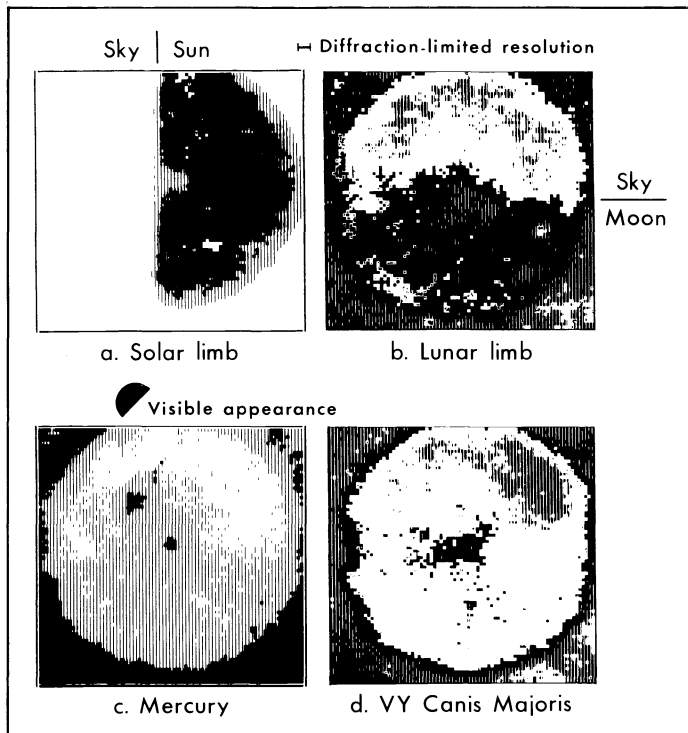


Figure 7. Infrared images of a number of astronomical objects from the work of Boyd.²⁹ Computer-generated plots of digitized photographic negatives are shown. In each case the field of view is round, and a spurious spot is introduced at the center of the field from the hole in the collimating mirror shown in Figure 6. Note the enhancement in the signal from the subsolar point on Mercury. The detection of VY Canis Majoris is marginal.

Future of Upconversion in Astronomy

It is clear that to date upconversion has not proved to be a particularly useful technique in astronomy. Only the very brightest infrared celestial sources can even be detected with existing upconversion systems, and no spectroscopic information has yet been obtained from these studies. However, upconversion methods have steadily improved in their sensitivity and it is likely that the technique will continue to improve. It seems useful to list here some of the advantages and some of the limitations of upconversion detection systems, and to study the possible improvements in upconversion techniques that seem possible at this time.

Since the time of the early suggestions¹⁰ that upconversion be used in infrared detection systems, infrared photoconductive detectors have become increasingly more sensitive, and thus the potential competitive advantage of upconversion systems in terms of NEP is limited. Upconversion systems do have the inherent advantage that they need not be cooled to cryogenic temperatures, in contrast to most other low noise infrared systems.

Should upconversion systems become comparable with other infrared systems in terms of their sensitivity, this ease of operation could make upconverters the preferred infrared detectors. Furthermore, most upconverters have an inherently narrow infrared bandpass, and if spectral information regarding an astronomical source is desired no additional losses need be suffered by using a monochromator in front of the detector.

Upconversion systems appear most attractive in terms of infrared imaging. With the exception of the work of Westphal et al³⁰, infrared imaging devices are still not common instruments in astronomy, due mainly to the expense of two-dimensional detector arrays and mechanical instabilities in raster scanning systems. More sensitive, diffraction limited infrared imaging upconverters could easily outperform other infrared systems for high angular resolution work.

One possible direction for further improvements in upconversion techniques would be the elimination of the unexplained noise source that has afflicted several workers, as discussed previously in this article. Since these noise sources do not seem to be of a fundamental nature, they can probably be eliminated, perhaps with the fabrication of more perfect crystals.

Conversion efficiency is proportional to laser power per unit area for the standard upconverter utilizing three-wave mixing; for the four-wave mixing technique of Bloom et al²², the conversion efficiency scales as the square of this quantity. A significant improvement in upconverter performance could be achieved by the development of cw laser sources in the 10 to 40 watt range, or higher, as opposed to the 1 to 4 watt range currently available. If tunable lasers of such power become available, the resonant techniques of Bloom et al²² and Bethune et al²⁴ may be exploited for astronomical applications.

Conversely, a significant improvement could be realized with existing laser systems if crystals with a larger nonlinear coefficient d became available. It should be recalled that the conversion efficiency depends on the square of d . The properties of a number of crystals of interest in upconversion studies are listed in Table 1. KDP, used in many of the early experiments in nonlinear optics, is included for comparison. Of the rest, only lithium niobate, lithium iodate and proustite have been used in upconverters for astronomy. It will be noted that several of the other materials have values of d significantly larger than those of the crystals currently being employed in astronomical upconverters. Cinnabar could potentially provide a factor of 4 improvement in quantum efficiency over proustite, and ZnGeP_2 could provide a factor of 25 improvement. Neither of these crystals is currently available in large samples with good transmission, but with sufficient work they could perhaps be fabricated. CdGeAs_2 has a nonlinear coefficient which predicts a conversion efficiency 400 times greater than that of proustite. This crystal is not transparent in the visible, and thus is not of use for upconversion. Its large value of d is very suggestive, however, that significant improvement in mixing crystals is possible.

Furthermore, it should be noted that the resonantly enhanced gas phase upconversion techniques of Bloom et al²² and Bethune et al²⁴ have hardly been exploited for sensitive infrared detection, and significant improvements in upconverter sensitivity may be realized by these methods.

Acknowledgments

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Table 1. Properties of Some Nonlinear Crystals of Interest in Upconversion

Name of Crystal	Crystal Point Group	Approximate Transparency Range (μm)	Refractive Index n_o at $1\ \mu\text{m}$	Birefringence $n_e - n_o$ at $1\ \mu\text{m}$	Measured Values of d in units of 10^{-9} esu	Reference Number
Potassium dihydrogen phosphate (KDP)	$\bar{4}2m$	0.2–1.0	1.5	–0.0397	$d_{36} = 1.5 \pm 20\%$	31
Lithium niobate (LiNbO_3)	3m	0.4–4.5	2.2487	–0.084	$d_{15} = 18 \pm 35\%$ $d_{22} = 10 \pm 35\%$	32
Lithium iodate (LiIO_3)	6	0.3–5.5	1.8517	–0.1349	$d_{31} = 17 \pm 30\%$	33
Proustite (Ag_3AsS_3)	3m	0.6–13	2.8264	–0.2362	$d_{31} = 40$ $d_{22} = 60$	34
Pyragyrite (Ag_3SbS_3)	3m	0.7–13	2.973	–0.152	$d_{31} = 30 \pm 30\%$ $d_{22} = 32 \pm 30\%$	35
Cinnabar (HgS)	32	0.6–15	2.7120	+0.293	$d_{11} = 120 \pm 30\%$	36
Zinc germanium phosphide (ZnGeP_2)	$\bar{4}2m$	0.75–12	3.2478	+0.0476	$d_{14} = 270 \pm 45\%$	37
Cadmium germanium arsenide (CdGeAs_2)	$\bar{4}2m$	3–17	---	---	$d_{14} = 1100 \pm 50\%$	38

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