1991

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The phenomenon of electric field induced (EFI) emission is examined in several diatomic and polyatomic molecules. The possibility of using this phenomenon as a diagnostic tool to measure, nonintrusively, the strength and direction of local electric fields in plasmas is discussed. An estimate of the EFI signal emitted in a typical application plasma is given. This yields a lower bound on the detector sensitivity necessary to exploit EFI emission in practical applications. It is concluded that, at present, the EFI signal could be measured by some very sensitive infrared detection schemes available. Current progress in infrared detector technology, if maintained, could result in the possibility of utilizing EFI emission on a more routine basis. This would allow measurement of electric fields in plasmas of species that are not suitable candidates for any of the other currently available schemes which measure such fields.

I. INTRODUCTION

A fundamental understanding of transport phenomena in gaseous discharges and plasmas depends critically upon a knowledge of the temporal and spatial dependence of the local electric field vector E, via the ratio E/N. In practical applications (such as microelectronics, plasma processing, etc.) control over E/N translates into control over the process in question (for example, the etched profile in the etching process). It has long been recognized that Langmuir probe measurements, besides being intrusive in nature, cannot be utilized in reactive plasmas used in etching and thin film deposition. Further, interpretation of the measurements obtained is usually difficult and requires assumptions, made in probe theories, that are generally invalid under the experimental conditions.

There are several successful techniques for nonperturbative measurements of local E fields that have been developed in the last few years. Moore, Davis, and Gottscho[1] used laser-induced fluorescence from rotational levels of BC1, in which parity mixing occurs under the influence of an electric field, to obtain sensitive (40 V/cm), nonintrusive, *in situ*, measurements of the local field with high spatial resolution ($\leqslant 10^{-4}$ cm^3). Doughty, Lawler, and Salih[2] measured discharge electric fields by optogalvanic detection of Rydberg atoms, utilizing the linear Stark effect. Kelleher, Delpech, and Weiner[3] measured a broadening of a valence autoionization resonance in strontium, which occurs because of an electric field dependent mixing with a broader state of opposite parity. Ganguly and Garscadden[4] have used Rydberg polarization spectroscopy to measure the direction of the local electric field. More work along these lines has been performed by these and other researchers.[5]

This paper investigates the possibility of using electric field induced (EFI) emission as a tool for nonintrusive measurements of local electric field vectors in discharges and plasmas containing diatomic or polyatomic species which have Raman allowed, but infrared forbidden vibra-

tional transitions. We first briefly discuss the phenomenon of EFI spectra in homonuclear diatomic molecules. The connection between EFI spectra and the Raman effect is emphasized and this is used to extend the discussion of EFI in diatomic molecules to polyatomics. The connection to the Raman effect shows that the best candidate vibrational modes would be totally symmetric, Raman active, infrared inactive, vibrational modes of polyatomic molecules. Several polyatomic molecules such as CCl_4, C_2Cl_4, C_2Br_4, and SF_6 are examined. An estimate for the emitted photon flux in a "typical" plasma is given. It is found that the emitted EFI signal could be measured with the most sensitive infrared detectors currently available. We conclude that the EFI emission scheme could become an important method for nonintrusive measurements of local electric fields in plasmas, if the rate of recent progress in infrared detection technology (for instance, in the development of metal oxide semiconductor photomultipliers[6]) is sustained. EFI emission would then offer a method for probing species that are not suitable candidates for any of the other current techniques.

II. ELECTRIC FIELD INDUCED (EFI) SPECTRA

The discussion below is carried out using a homonuclear diatomic molecule as an example. An analogous argument applies to any normal vibrational mode of a polyatomic molecule which is Raman active, but infrared inactive.

It is well known that symmetric diatomic molecules, not possessing an electric dipole moment, do not exhibit an infrared vibration-rotation spectrum. However, as Condon[7] first pointed out, when an external electric field is imposed upon such molecules they become infrared active by virtue of induced dipole moments. This can be explained as a limiting case of the Raman effect.

In the latter, an electromagnetic wave at frequency ω interacts with a molecule in such a way that the scattered

light has weak components at frequencies different from the main (Rayleigh) scattered beam whose frequency remains unchanged at ω. The inelastically scattered beam contains frequencies $\omega + \omega_v$, where ω_v is the vibrational frequency of the molecule. Such an effect occurs because the electronic polarization of a molecule generally depends on the bond length and is therefore modulated at the vibrational frequency. Since the induced polarization, p, is proportional to both the polarizability and the E field of the e-m wave, p exhibits, in addition to the main component at ω, beat frequencies $\omega \pm \omega_v$, leading to the observed Raman effect. In the limit that the e-m wave frequency tends to zero, the molecule will emit or absorb light of the vibrational frequency ω_v. Hence, infrared absorption and emission spectra are induced, and the EFI effect obeys the Raman selection rules $\Delta v=0$, ± 1; $\Delta j=0$, ± 2.

An effect intimately connected to the EFI effect, the collisionally induced dipole moment (CID) effect, in which an induced dipole moment occurs during collisions between homonuclear diatomic molecules, was first observed experimentally by Crawford, Welsh, and Locke[8] and subsequently investigated by others.[9] EFI absorption spectra in H_2 were first measured by Crawford and Dagg[10] and subsequently also investigated by Buijs and Gush.[11] Courtois and Jouve[12] measured the EFI absorption spectrum of N_2. Such spectra were measured in polyatomic molecules a year later by Jones.[13]

The intensity of the EFI spectrum depends on the square of the external field strength, and could, therefore, be used to measure the distribution of the field in an electric discharge containing a molecule such as N_2, O_2, or a polyatomic such as SF_6. Fluorescence measurements have an advantage over absorption spectral measurements in that the signal, albeit weak, would be compared to an essentially zero background signal. This would be counterbalanced by the need to populate excited vibrational states. However, in a gaseous discharge, vibrational excitation by electron impact can be quite efficient. Some examples, including N_2 and SF_6, are discussed below.

III. FIELD-INDUCED INFRARED FLUORESCENCE

The spontaneous emission lifetime of a transition between two levels, i and f, is given by the reciprocal of the Einstein A coefficient, which itself is related to the dipole moment matrix element, μ_{fi}, coupling the two levels through the following relation[14]

$$A_{fi}=\frac{64}{3c^3h}\pi^4\nu^3\frac{1}{4\pi\epsilon_0}\mu_{fi}^2.$$ (1)

Here,

$$\mu_{fi}=\langle\psi_f|p|\psi_i\rangle,$$ (2)

and, in the present context, represents the induced dipole moment

$$\mu_{fi}=\epsilon_0E\langle\psi_f|\alpha|\psi_i\rangle.$$ (3)

The polarizability, α, can be expanded in a Taylor series:

$$\alpha\simeq\alpha_0+\left(\frac{\partial\alpha}{\partial Q_0}\right)Q,$$ (4)

where α_0 is the polarizability of the molecule at its equilibrium bond length, $(\partial\alpha/\partial Q)_0$ is the derivative evaluated at this bond length, and Q is the vibrational normal coordinate.

We now outline the significance of Eq. (4) for the present discussion. As mentioned before, one might view the EFI effect as a limiting case of the Raman effect.[7] In the usual Raman effect an incident electromagnetic wave with frequency ω is scattered inelastically by a molecule, resulting in radiation at $\omega \pm \omega_v$. ω_v is the frequency of the appropriate molecular vibrational mode. The EFI effect is the Raman effect with $\omega = 0$.[7] Now, since only the second term in Eq. (4) leads to the Raman effect (the first term, i.e., α_0, represents Rayleigh scattering), it follows that for the EFI effect under consideration, only this (second) term need be considered.

The Einstein A coefficient relevant to the EFI effect then becomes

$$A_{if}=\frac{64}{3c^3h}\pi^4\nu^3\frac{1}{4\pi\epsilon_0}\epsilon_0^2\left|\langle\psi_f|\left(\frac{\partial\alpha}{\partial Q}\right)_0Q|\psi_i\rangle\right|^2E^2.$$ (5)

The matrix element term, $|\langle\psi_f(\partial\alpha/\partial Q)_0Q|\psi_i\rangle|^2$, has to be ultimately obtained experimentally. For N_2, this can be deduced from the experimental work of Courtois and Jouve.[12] This value ($\simeq 10^{-25}cm^3$) leads to

$$A_{if}\simeq3\times10^{-22}E^2\text{ sec}^{-1}.$$ (6)

for N_2, where E is in volts per meter.

If the density of the excited vibrational state is known, an estimate for the expected fluorescence intensity can be obtained. Hence, if, for simplicity, a steady state condition is assumed, the density of vibrationally excited molecules, N_i, will be given by

$$N_i\simeq\frac{r}{A_{if}+K_l},$$ (7)

where r is the rate at which excitation occurs (for example by electron impact) and K_l is the rate of radiationless deactivation.

If emission from a volume $\Delta V=A\Delta l$ is monitored, then

$$I_{em}=h\nu\,\Delta l\frac{r}{1+(K_l/A_{if})}.$$ (8)

Here, $h\nu$ is the infrared photon energy corresponding to the vibrational energy level spacing.

The rate of excitation of vibrationally excited molecules, r, is a complicated function of the conditions in the discharge (mainly the reduced field strength—E/N), the molecular species, and the discharge constituents. For simple diatomics such as N_2, CO, O_2, Nighan[15] has obtained the power transferred, η, to the vibrational and electronic states as a fraction of the Joule heating term H.

Since $r = (\eta/\Delta E) H (1/\Delta V)$ cm^{-3} sec^{-1}, where H is the power deposited in the volume ΔV, ΔE, the vibrational quantum ($\Delta E = h\nu$), and η the fractional power transferred to the excited vibrational states, it follows that

$$I_{em} = \frac{\eta H}{A} \frac{1}{1 + (K_l/A_{if})} \frac{W}{m^2}. \qquad (9)$$

In Eq. (9) η, H, and A_{if} are all functions of E. The factor $(\eta H/A)$ represents that part of the power per unit area in the discharge that results in vibrationally excited molecules. The fraction $1/[1 + (K_l/A_{if}]$ represents the effect of competition between the radiative (A_{if}) and nonradiative (K_l) processes that lead to a depletion of these excited states. Clearly, if nonradiative losses were zero ($K_l = 0$), all the power (per unit area—$\eta H/A$) deposited in the vibrationally excited species would be emitted. Conversely, if the nonradiative losses are overwhelmingly large in comparison to the rate of spontaneous emission, then no fluorescence signal will be seen. The nonradiative losses, represented by K_l, will mostly involve degradation of the vibrational energy into heat, via vibrational-translational ($V \rightarrow T$) conversion. For pure N_2, the $V \rightarrow T$ relaxation time, at 1 atm, corresponds to $K_l \cong 5 \times 10^4$ sec^{-1}; for O_2, the corresponding value is about two orders of magnitude smaller. Since the deactivation rate is proportional to the number of collisions per unit time, the value of K_l is approximately 50 sec^{-1} (Ref. 16) for the relatively low (approximately 1 Torr) pressures in the discharges being considered here. In this case, then, Eqs. (6) and (9) lead to

$$I_{em} \leqslant \frac{(\eta H/A)}{(1 + 10^{23}/E^2)},$$

for N_2. For $E^2 \ll 10^{23} V^2/m^2$, this becomes

$$I_{em} \leqslant (\eta H/A) 10^{-23} E^2.$$

It is important to note that, in practice, the measured emission intensity, I_{em}, would be the result of an electric field viewed over a finite path length. Hence, E in the above expression will be, at best, a line-averaged quantity. The method under discussion could only yield values of E at a given point if E was approximately constant over the line of sight (i.e. if E was constant over Δl). While this may be true in specific instances where the spatial variation of E might exhibit some symmetry, E will not, in general, be constant over Δl. In the latter case, then, one would actually be measuring an average such as $(1/\Delta L)\int_0^{\Delta L} E^2 dl$. It should be pointed out, however, that this limitation is not a fundamental one. One could, in principle, extract values of the E fields at specific points by deconvolving results of line-averaged measurements over several different paths.

We note that $(\eta H/A)$ would be some function of E, and estimates for this factor could be obtained by a numerical analysis of the Boltzmann equation such as that carried out by Nighan.[15] $\eta H/A$ is in the range 10^{-2}–1 W/cm^2, yielding, for $E = 1$ KV/cm, I_{em} between 10^{-13}–10^{-15} W/cm^2. This corresponds to approximately 10^4–10^6 photons cm^{-2} sec^{-1}, at the wavelength corresponding to the N_2 fundamental.

The EFI signal will compete with background noise from free-free bremsstrahlung and free-bound recombination radiation. For the conditions in a typical discharge such as those being considered here, recombination radiation will be greater than free-free bremsstrahlung.[17] A rough estimate of the recombination radiation intensity can be made[17] from

$$\frac{dE_{fb}}{d\nu} = CN_e N_{i+1} \left(\frac{\chi_H}{kT_e}\right)^{3/2} \left(\frac{\chi_{i,n}}{\chi_H}\right)^2 \left(\frac{\eta_n}{n}\right) g_{bf}$$

$$\exp[(\chi_{i,n} - h\nu)/kT_e], \qquad (10)$$

which gives the intensity of emission per cc per second in a unit frequency interval from recombination into the nth shell of a hydrogen-like ion of charge i. Here, N_e and N_{i+1} are the densities of the electrons and ions of charge $(i + 1)$, T_e is the electron temperature, $\chi_{i,n}$ is the ionization potential from the final state, η_n is the number of places in the nth shell which can be occupied by the captured electron, g_{bf} is the bound-free Gaunt correction factor, and $C = 1.7 \times 10^{-40}$ erg cm^3.

If one assumes $N_e \cong N_{i+1} \cong 10^8$ cm^{-3}, $kT_e = 1$ eV, $\chi_{i,n} = 5$ eV, $\eta_n = 5$, $h\nu = 0.25$ eV, then one obtains, in the present case, a recombination emission photon flux of 8×10^3 cm^{-2} sec^{-1}. Hence, for such plasmas, (10) implies that the EFI signal (10^4–10^6 photons cm^{-2} sec^{-1}) will be easily distinguishable from the background recombination and bremsstrahlung continuum.

We note, further, that Eq. (10) assumes thermodynamic equilibrium and, therefore, may be an overestimate of the recombination radiation intensity. In the cathode fall region, where high electric fields on the order of magnitude assumed in the above estimate exist, the conditions are of a highly nonequilibrium nature. The cathode fall region is expected to be "darker" than predicted in Eq. (10). Hence, it might be possible to measure such fields in plasmas with electron densities greater than the 10^8 cm^{-3} assumed above.[18] Many glow discharge sputtering and plasma etching environments have electron densities on the order of 10^{10}cm^{-3} (Ref. 18). Here, the recombination continuum intensity will be greater than our estimate above. However, in the cathode fall region this background may still be sufficiently lower than the EFI emission signal. We note in this regard that even if the background emission is comparable to the signal it would still be possible to distinguish between the two by performing intensity measurements over a range centered around the EFI emission wavelength. Such a technique would work because the signal is essentially a line, while the background is broad band.

While the signal photon intensity is low, it could be measured by currently available infrared detectors. Hence, for example, He3 bolometers, operating at 0.3 degrees K, are capable of measuring photon fluxes of between 10^6 and 10^7 per cm^2 per sec.[19] It is clear, nonetheless, that the technique described in this paper would benefit from progress in the field of infrared detection. Along these lines, one should note that progress in the technology of

metaloxide-semiconductor photomultipliers (MOSPM), which show great promise,[6] is especially encouraging.

IV. EFI-INDUCED SPECTRA IN POLYATOMIC MOLECULES

An alternative way to describe the EFI effect in homonuclear diatomics is to say that vibrations in such molecules are infrared-inactive (i.e., do not exhibit an electric dipole infrared spectrum but are Raman-active, i.e., exhibit such a spectrum in the presence of an external electric field—a static one in the discussions above). It follows that, to extend the above discussion to polyatomic molecules, one should look for normal modes of vibration which are Raman active,[20] but infrared inactive. Group theoretical arguments[21] show that such vibrational modes are those species for which the polarizability tensor components (α_{ij}, $i = x,y,z$; $j = x,y,z$) form a basis, but for which the electric dipole moment components (μ_x, μ_y, μ_z) do not. Further, since the polarizability components transform as x^2, y^2, z^2, xy, etc.,[22] and the dipole moment components transform as x,y,z the appropriate normal vibrational modes can be found from the character table of the point group to which the molecule belongs.

With the diagnostic application in mind, one wants a normal vibrational mode which shows a large intensity in the Raman effect. Since it is known[23] that totally symmetric vibrational modes exhibit the strongest Raman lines, we restrict ourselves to a discussion of only such normal modes in this section (although, in principle, this is not necessary). The point groups of interest are, therefore, the $D_n, D_{nh}, D_{nd}, C_{nh}, S_n$ groups, all the cubic groups (T, T_h, T_d, O, and O_h), and the icosahedral group I_h as well as C_i and $D_{\infty h}$. [Note all point groups which have an inversion center ($C_i, C_{2h}, C_{4h}, C_{6h}, D_{2h}, D_{4h}, D_{6h}, D_{8h}, D_{3d}, D_{5d}, S_6, T_h, O_h, D_{\infty h}$, and I_h) to which the principle of mutual exclusion[20] applies (no infrared active transition may be Raman active and vice versa) form a subset of this list.]

The molecules listed in Table I have totally symmetric vibrational modes, denoted by v_1, which are forbidden in the ir spectrum but are Raman allowed. From a practical point of view it is desired that there not be any strong infrared allowed fundamental, overtone, or combination lines in the near proximity of the Raman-active v_1 mode. This means that molecules such as acetylene (in which the ir allowed v_3 line is very strong and near v_1), methane (in which the ir allowed v_3 line is near v_1), ethylene (in which the strong ir allowed v_9 line is near v_1) are not suitable candidates.

Among the promising molecules from the incomplete list given in Table I are N_2 and SF_6. N_2 has been discussed above in Sec. III. We briefly discuss SF_6 now.

This molecule belongs to octahedral point group O_h, the sulfur atom being at the center of the octahedron and the six fluorine atoms at the corners. The molecule possesses 15 normal modes of vibration, consisting of the totally symmetric "breathing" mode a_{1g}, a doubly degenerate mode e_g, and four triply degenerate modes t_{1u}, t_{1u}, t_{2g}, and

TABLE I. Some molecules with Raman-active, infrared inactive totally symmetric vibrational normal modes.

	Molecule	Point group	Vibrational modes			Comments
				Raman-active	ir active	
Diatomics	O_2	$D_{\infty h}$	v_1:1580 cm^{-1}	v_1		
	N_2	$D_{\infty h}$	v_1:2359 cm^{-1}	v_1		Efficient excitation of vibrational
	H_2	$D_{\infty h}$	v_1:4395 cm^{-1}	v_1		mode by e-impact; N_2 used as a store of vibrational energy
Triatomics	CO_2	$D_{\infty h}$	$v_1(\sigma_g^+)$:1300 cm^{-1}	v_1	v_{2a}, v_{2b}	The v_1 line appears as a doublet
			$v_{2a}, v_{2b}(\pi_u)$:667 cm^{-1}		v_3	(1285 cm^{-1}, 1388 cm^{-1}) be-
			$v_3(\sigma_u^+)$:2350 cm^{-1}			cause of Fermi Resonance
	CS_2	$D_{\infty h}$	$v_1(\sigma_g^+)$:656.5 cm^{-1}	v_1	v_{2a}, v_{2b}	
			$v_{2a}, v_{2b}(\pi_u)$:396.5 cm^{-1}		v_3	
			$v_3(\sigma_u^+)$:1523 cm^{-1}			
Four-atomic Molecules	C_2H_2 (acetylene)	$D_{\infty h}$	$v_1(\sigma_g^+)$:3373 cm^{-1}	v_1, v_2, v_4	v_3, v_5	v_1 and v_2 strong in Raman
			$v_2(\sigma_g^+)$:1973 cm^{-1}			spectra, v_4 weak, v_3 ir allowed
			$v_3(\sigma_u^+)$:3287 cm^{-1}			and very strong; also v_3 and v_1
			$v_4(\pi_g)$:611.8 cm^{-1} (doubly degenerate)			in close proximity
			$v_5(\pi_u)$:729 cm^{-1} (doubly degenerate)			
	BF_3	D_{3h}	$v_1(a_1')$:888 cm^{-1}	v_1, v_{3a}, v_{3b}	v_2, v_{3a}, v_{3b}	
			$v_2(a_2'')$:691 cm^{-1}	v_{4b}	v_{4a}, v_{4b}	
			$v_{3a}, v_{3b}(a')$:1446 cm^{-1}	v_{4a}		
			$v_{4a}v_{4b}(a')$:480 cm^{-1}			
			$v_1(a_1)$:2911 cm^{-1}; $v_{2a}, v_{2b}(a)$:1526 cm^{-1}	v_1, v_{2a}, v_{2b}	v_{3a}, v_{3b}, v_{3c}	
Five-atomic Molecules	CH_4	T_d	$v_{3a}, v_{3b}, v_{3c}(t_2)$:3020 cm^{-1};	v_{3a}, v_{3b}, v_{3c}	v_{4a}, v_{4b}, v_{4c}	
			$v_{4a}, v_{4b}, v_{4c}(t_2)$:1306 cm^{-1}	v_{4a}, v_{4b}, v_{4c}		
			$v_1(a_1)$:459 cm^{-1}; $v_{2a}, v_{2a}(a)$:218 cm^{-1},	v_1, v_{2a}, v_{2b}	v_{3a}, v_{3b}, v_{3c}	
	CCl_4	T_d	$v_{3a}, v_{3b}, v_{3c}(t_2)$:782 cm^{-1};	v_{3a}, v_{3b}, v_{3c}	v_{4a}, v_{4b}, v_{4c}	
			$v_{4a}, v_{4b}, v_{4c}(t_2)$:314 cm^{-1}.	v_{4a}, v_{4b}, v_{4c}		

TABLE I. (continued).

	Molecule	Point group	Vibrational modes			Comments
Six-atomic Molecules	C_4H_2 Diacetylene	$D_{\infty h}$	$\nu_1(\sigma_g^+)$ $\nu_2(\sigma_g^+)$ $\nu_3(\sigma_g^+)$ $\nu_4(\sigma_u^+)$ $\nu_5(\sigma_u^+)$ $\nu_6(\pi_g)$ $\nu_7(\pi_g)$ each $\nu_8(\pi_u)$ doubly $\nu_9(\pi_u)$ degenerate [Ref. 23, p. 324]	ν_1,ν_2,ν_3 ν_6,ν_7	ν_4,ν_5,ν_8,ν_9	
	C_2	D_{2h}	$\nu_1(a_g)$:3019 cm^{-1};$\nu_2(a_g)$:1623 cm^{-1}; $\nu_3(a_g)$:1342 cm^{-1};$\nu_4(a_u)$:825 cm^{-1} $\nu_5(b_{1g})$:3272 cm^{-1};$\nu_6(b_{1g})$:1050 cm^{-1} $\nu_7(b_{1u})$:949 cm^{-1};$\nu_8(b_{2g})$:943 cm^{-1}; $\nu_9(b_{2a})$:3105 cm^{-1}; $\nu_{10}(b_{2u})$:995 cm^{-1} $\nu_{11}(b_{3u})$:2989 cm^{-1}; $\nu_{12}(b_{3u})$:1443 cm^{-1}	ν_1,ν_2,ν_3 ν_5,ν_6,ν_8	$\nu_7,\nu_9,\nu_{10},\nu_{11},$ ν_{12}	ν_4 is inactive, $\nu_1,\nu_2,\nu_3,$ the totally symmetric modes are very strong Raman lines. There is a strong ir line (ν_9 near ν_1; and another ir strong line (ν_{12}) near ν_2 and ν_3. This makes the molecule an unsuitable candidate.
	C_2Cl_4 Tetrachloroethylene	D_{2h}	$\nu_1(a_g)$:1571 cm^{-1};$\nu_2(a_g)$:447 cm^{-1} $\nu_3(a_g)$:237 cm^{-1}; $\nu_4(a_u)$: $\nu_5(b_{1g})$:1000 cm^{-1}; $\nu_6(b_{1g})$:337 cm^{-1} $\nu_7(b_{1u})$:332 cm^{-1}; $\nu_8(b_{2g})$:512 cm^{-1}; $\nu_9(b_{2u})$:909 cm^{-1};$\nu_{10}(b_{2u})$:213 cm^{-1} $\nu_{11}(b_{3u})$:782 cm^{-1}; ν_{12}:418 cm^{-1}	Ditto	Ditto	EFI induced absorption spectrum measured experimentally by Jones.
	C_2Br_4 Tetrabromoethylene	D_{2h}	Species as in C_2H_4 and C_2Cl_4	Ditto	Ditto	Ditto
	Diphenyl acetylene	D_{2h}	Ditto	Ditto	Ditto	Ditto
Seven-atomic Molecules	SF_6	O_h	$\nu_1(a_{1g})$:775 cm^{-1} (12.9 μ) $\nu_{2a},\nu_{2b}(l_g)$:644 cm^{-1} (15.5μ) $\nu_{3a},\nu_{3b},\nu_{3c}(t_{1u})$:965 cm^{-1} (10.3 μ) $\nu_{4a},\nu_{4b},\nu_{4c}(t_{1u})$:617 cm^{-1} (16.2 μ) $\nu_{5a},\nu_{5b},\nu_{5c}(t_{2g})$:524 cm^{-1} (19.1 μ) $\nu_{6a},\nu_{6b},\nu_{6c}(t_{2u})$:363 cm^{-1} (27.5 μ)	$\nu_1,\nu_{2a},\nu_{2b},\nu_{5a},$ ν_{5b},ν_{5c}	$\nu_{3a},\nu_{3b},\nu_{3c}$ $\nu_{4a},\nu_{4b},\nu_{4c}$	$\nu_{6a},\nu_{6b},\nu_{6c}$ are inactive. The totally symmetric mode ν_1 appears as a strong line in the Raman spectrum and is sufficiently far removed from the strong ir active modes ν_3,ν_4. There are no strong overtones or combinations near ν_1 and this mode (as well as ν_3) is efficiently excited by electron impact.

t_{2u}.[23] The fundamentals of these species are designated as ν_1, ν_2, ν_3, ν_4, ν_5, and ν_6, respectively. The ν_1, ν_2, and ν_5 fundamentals are forbidden by the electric dipole selection rule, however they are all Raman active. The ν_3 and ν_4 modes are ir active but Raman inactive. The final fundamental, ν_6, is neither infrared nor Raman active.

Being totally symmetric, the ν_1 mode appears as a very strong line in the Raman spectrum.[23] Also, there are no strong infrared fundamentals, overtones, or combinations near this frequency. This fundamental can therefore be expected to appear as an EFI line and would be fairly distinct.

The ν_1 mode would be a suitable candidate for monitoring EFI fluorescence in a discharge because it is one of the two modes that are efficiently excited by electron impact. The other mode is the strongly infrared-active ν_3 mode. Rohr's[24,25] results indicate that the integrated total vibrational excitation is about 10^{-15}cm^{-2}, being about 1.5 times the elastic cross section. The vibrational excitation cross section is dominated by the ν_1 and ν_3 modes, with some excitation of the infrared active ν_4 mode also occurring. The ν_3 (10.3μ) and ν_4 (16.2μ) fundamentals are sufficiently removed from ν_1 (12.9μ) so as not to interfere with any EFI fluorescence. As discussed above, the noise at 12.9μ that would have to be overcome would be principally from recombination radiation.

V. DISCUSSION

A possible experimental arrangement is shown below in Fig. 1. An electron beam would produce vibrationally excited molecules. The sample chamber would hold the molecule under investigation, in a rare gas buffer. Infrared emission (at the fundamental lines given in Table I) would be monitored, in the presence and absence of an electric field.

The EFI emission intensity is given by

$$I_{em} = K\Delta l/h\nu N_i E^2, \qquad (11)$$
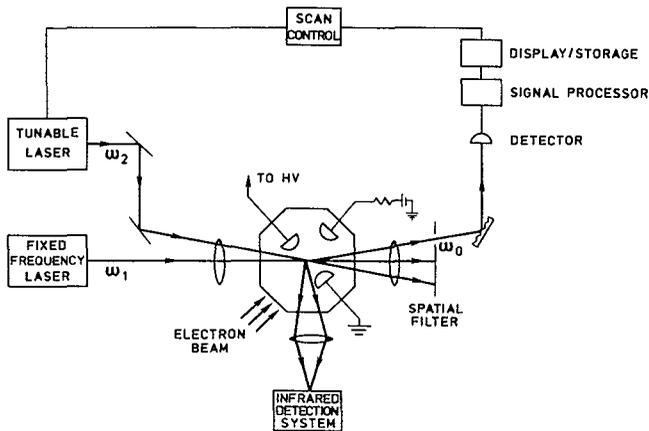
FIG. 1. Proposed experimental arrangement.

FIG. 2. Depolarization measurements in Raman scattering.

where K is the factor on the right-hand side of Eq. (5) which multiples E^2, Δl the path length being monitored, and N_i the density of excited vibrational levels produced. K depends on the molecular transition being monitored through the induced dipole moment matrix element. The vibrationally excited state density, n_i, could be measured by Coherent Antistokes Raman Spectroscopy (CARS).

From the viewpoint of a diagnostic application, we note that Eq. (11) yields

$$E_1 = E_0 \left(\frac{I_{\mathrm{em}_1}}{I_{\mathrm{em}_0}} \right)^{1/2} \left(\frac{\Delta l_0}{\Delta l_1} \right)^{1/2} \left(\frac{N_{i0}}{N_{i1}} \right)^{1/2}, \qquad (12)$$

where the subscript 1 denotes values relevant to the condition in which the local electric field is to be measured, and the subscript 0 denotes values that would be obtained in a calibration experiment to be conducted in an apparatus such as that shown in Fig. 1. In the calibration experiment E_0 would be known because the experiment would be conducted with a high impedance in series with the electrodes so as to prevent a discharge. Equation (12) shows that, then, it is necessary to obtain only the ratios of the measured intensities and excited state population densities in order to find the local electric field strength to be measured, E_1. A measurement of such a ratio could be obtained by a CARS type arrangement, such as that depicted in Fig. 1. The latter is an adaptation of a standard CARS setup (see, for example, Ref. 26).

The EFI effect can be viewed as a limiting case (with the frequency of incident radiation equal to zero) of Raman scattering and, hence, obeys the Raman selection rules. EFI absorption and the process leading to the Stokes Raman line are analogous, because in both cases, a molecule initially in the ground state makes a transition to an excited vibration-rotation level after interacting with an electromagnetic field. On the other hand, EFI emission and the antistokes Raman process are analogous because in both these cases a molecule, initially in an excited vibration-rotation level makes a transition to a lower level, under the influence of an electromagnetic field and contributes a quantum of energy to the latter. The close analogy
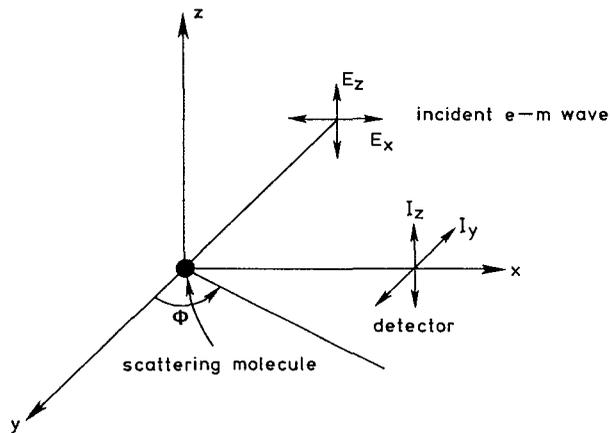
between the EFI and Raman effects means that, in principle, the direction of the electric field could be determined by measurement of depolarization ratios.

In the Raman effect (see Fig. 2) when the incident beam is polarized in a direction perpendicular to the direction of scattering (i.e., $E_x = 0$), the depolarization ratio is given by

$$\rho_{P\perp} = \frac{I_y}{I_z} = \frac{6\gamma_{\mathrm{nm}}^2}{45(\alpha_{\mathrm{nm}})^2 + 4\gamma_{\mathrm{nm}}^2}, \qquad (13)$$

where α_{nm} and γ_{nm} are, respectively, the matrix elements of the mean value and anisotropy invariants of polarizability. Equation (13) also applies to emission induced by a static electric field, pointing along the z axis, as in Fig. 2. In this case, because of symmetry, the depolarization ratio would be independent of the azimuthal angle ϕ. This would provide a means for determining the direction of the electric field. For instance, the measurement of a constant depolarization around 2π radians in a given circle centered on the scatterer indicates that the E field is perpendicular to this plane. (Once again, as mentioned in Sec. III, this discussion regarding extraction of information about the field direction from emission polarization measurements must be tempered with the realization that, in practice, the emission detected is an average over the line of sight, Δl. Hence, this simplified discussion applies, strictly speaking, to only those lines of light over which the E field vector, i.e., its magnitude as well as direction are constant.)

The technique of EFI fluorescence could, in principle, be extended to measurements in the liquid as well as solid phases. For example, the fundamental optical lattice vibrational mode in crystals of octahedral symmetry O_h such as diamond, silicon, and germanium are infrared inactive but Raman allowed (cf. SF_6 in Table I). (Weak absorption bands, explained by the existence of higher order electric moments have been observed[27].) It might be possible to observe optical phonon transitions which become allowed in the presence of E fields and hence obtain a measurement of the latter.

In concluding, we note that an electric field intensity of 1 kV/cm (a value that might be expected in the cathode fall region of a discharge) would produce an EFI emission

photon flux of up to 10^6 photons/cm^2/sec. This is a level that can be detected by the sensitive infrared detectors currently available (for example the He 3 bolometer system). We note also that if sufficient progress occurs in infrared detector technology, EFI emission would be an attractive method for measuring local fields in plasmas of species that are not suitable candidates in other currently available diagnostic techniques.

ACKNOWLEDGMENTS

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