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THE EVALUATION OF SATURATED AMINES AS POTENTIAL ULTRAVIOLET LAS--ETC(U)

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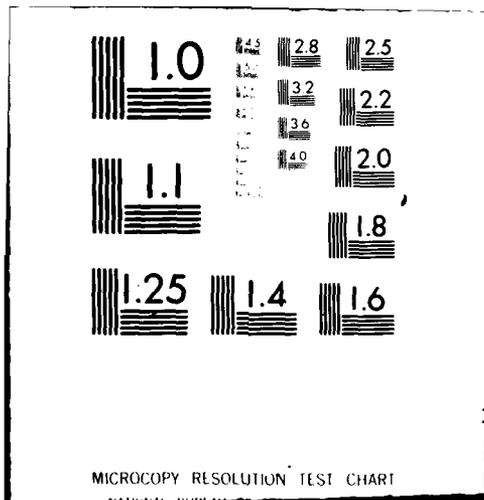
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The specific goal of the project as outlined in the proposal was to determine whether under various pump conditions saturated amines could be observed to lase in the expected ultraviolet (280 - 320 nm) region. A variety of chemical and physical systems was chosen in order to maximize the likelihood that lasing action could be produced and observed. While superradiant fluorescence was almost always detected under conditions of 249-nm KrF* laser irradiation, no evidence of amine lasing was obtained for any compound under any conditions (i.e. vapor		

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or condensed phase). For vapor phase systems, it was observed that extensive ionization current was produced consequent to laser pumping. While quantitative measurements of the ion yields were not performed, it is believed that the principle loss mechanism in the amine laser cavity is via up-pumping to an ion state of the parent (or fragment). Thus, despite the initially favorable prognosis of these compounds with respect to lasing action, i.e., relatively easily achievable threshold conditions, the up-pumping cross section of these compounds is apparently too large to allow for net amplification.

Further pursuit of the ionization process using multiphoton excitation led to the discovery that, in the vapor phase, two photon ionization produced coherently from a two photon populated electronic state (\tilde{A}) was induced with selectivity from various vibronic states in \tilde{A} . Thus the ionization cross section from the \tilde{A} (fluorescent) state is sharply modulated according to the vibronic character to the initially pumped state (in the $\tilde{A} \rightarrow X$ transition). The simultaneous measurement of the two photon-induced fluorescence, along with the multiphoton ionization current as a function of laser wavelength, was studied. This technique indicated those vibrational modes in the \tilde{A} -state which are particularly labile with respect to ionization. This state dependent depletion process was examined in detail for two amines, trimethylamine, and 1-azabicyclo(2.2.2)octane.

For both amines, significant distortions in the fluorescence excitation spectra were observed relative to the respective multiphoton ionization spectra which appeared to be 'normal' (i.e. consistent with the one photon absorption spectra). The analysis of these data shows that both dynamic information about intramolecular vibrational energy redistribution and structural information about the ion formed in the process can be obtained.

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Experimental Approach

Organic Materials

The amines examined are divided into three categories: (1) monofunctional amines having both medium and low intramolecular self quenching efficiencies, (2) bifunctional amines which undergo rapid intramolecular excimer formation, and (3) monofunctional amines which undergo intermolecular excimer formation. Amines representing all three categories were examined both in the vapor and condensed phases. For volatile amines, pressures varied between ca. 1 and 100 Torr. The medium chosen for solution studies was n-hexane; in this solvent, concentrations ranged from ca. 10^{-4} - 10^{-7} M.

Trial Laser Cavity

For simplicity and convenience it was decided to use a simple 1-cm square Suprasil fluorescence cell as the laser cavity. To one window, a small front surface mirror was attached using a film of hexadecane liquid; this acted as one end of the cavity. For most experiments, the normal reflectivity of the other window was used as the out-coupling device, although in a few experiments a partially transmitting mirror was used. The system was irradiated transversely using the cylindrically focused laser beam produced by a Lumonics multi-gas laser. In most cases the 249-nm line of the KrF* system was used, although both the 193-nm and 222-nm lines of the ArF* and KrCl* mixtures, respectively, were attempted. It was estimated that about 100 mJ of energy were produced in the 249-nm pulse.

In order to verify that the cavity used in the procedure was effective and that any lasing from the amine samples would be detected, p-terphenyl (in cyclohexane) was used as a lasing dye. When subject to 249-nm pumping by the laser, this dye produced an easily measurable lasing beam. Since the fluorescence produced by ordinary dye-brightened paper was sufficiently visible, this simple detector was used as the lasing criterion. No advantage was realized by using a Joulmeter as the dye laser beam detector.

Unfortunately no lasing action from any of the amines under any of the conditions listed above could be observed, and hence it was concluded that the loss in gain arising from one photon ionization from the \tilde{A} state was always too large to result in net amplification. This is consistent with the observations

of Zapka and Schäfer who demonstrated the efficacy of one photon ionization of the \tilde{A} state of trimethylamine vapor. The hope that the ionization cross section of the \tilde{A} state of structurally hindered amines (eg. tri-n-hexylamine) in solution would be low enough to permit the development of lasing was unrealized. In addition, the potential of the emissive excimer state (\tilde{X}) of amines, both intermolecular (1-azabicyclo(2.2.2)octane) and intramolecular (1,3-bis(dimethylamino)propane) as the lasing state of such molecules appeared to be negative. Thus the conclusion is reached that conditions cannot be found for the various saturated amine systems such that lasing action of the fluorescent states will result.

As a result of investigating whether the fluorescence was produced under the excitation conditions (it was), it was decided to also monitor total ion current. This approach led to an examination of the multiphoton ionization (MPI) spectrum of the amines using a focused tunable dye laser. The mechanism of ionization is two photon absorption to the A state of the amine followed by coherent one (or two) photon ionization of the parent ion (or possible higher order multiphoton-induced fragmentation/ionization).

The MPI spectrum was very easily obtained because of the large ionization currents produced. Under the identical irradiation conditions, fluorescence produced by the amines was also measurable. This fluorescence was also dispersed and was found to agree with the one photon-induced fluorescence spectrum. Such experiments were performed with two amines: trimethylamine (TMA) and 1-azabicyclo(2.2.2)octane (ABCO) -- both in the vapor phase. TMA was usually studied at pressures between 5 and 50 Torr, while the ABCO pressure was set by its partial pressure of ca. 2 Torr at ambient temperature.

The results of this study clearly demonstrate that the two photon fluorescence excitation (TPFE) spectra for both amines differ radically from the respective MPI spectra. In the case of TMA, where the MPI and one photon absorption (OPA) spectra are structureless, thus precluding a spectroscopically quantitative analysis to be made, the TPFE spectrum revealed structural features not observed in either the MPI or OPA spectrum. Because of the presence of rich vibronic detail in the MPI and OPA spectrum of ABCO, this molecule lent itself to a more quantitative analysis of the TPFE-MPI discrepancies.

This study appears in the January 1, 1982 issue of the Journal of Chemical Physics (76, 102). Reprints are appended to this report in order to provide the detailed results of this investigation. The implications of these observations

are far reaching. They point to a new technique for measuring the rates of intramolecular vibrational energy redistribution. Moreover, these rates may be determined for various vibrational modes which are excited in the \tilde{A} state of any emissive molecule. Essentially, the method relies on the pressure dependence of the TPF spectrum of a molecule and how the TPF spectrum converges (at higher pressures) to the MPI spectrum. The following section presents a kinetic argument showing how the pressure dependence of the TPF spectrum can be used to determine intramolecular vibrational energy redistribution rates.

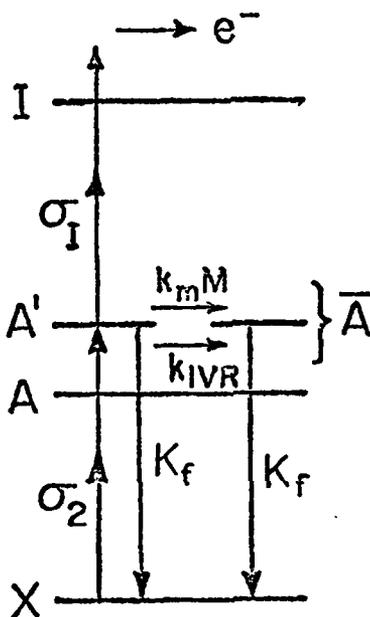
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The intensity alterations in the vibronic features in the TPF spectrum of ABCO are interpreted by Halpern et al. as arising from the vibrational mode dependence of laser up-pumping from the S_1 state to the ground state of the parent ion (and perhaps also to other ionic fragments). Thus according to this view, the TPF spectrum represents the net result of resonant two photon population of a single vibronic level (SVL) of the S_1 state, along with coherent depopulation of this level. A significant part of this picture, however, is that the coherent up-pumping process (i.e., the loss mechanism) can be interrupted, or quenched, by the intervention of two possible pathways: (1) intramolecular vibrational relaxation (or redistribution) (IVR) out of the initially prepared SVL, and (2) collisionally induced vibrational relaxation (VR) brought about by the intervention of an added buffer gas. The effect of (1) and/or (2) is, of course, to reduce the loss in the S_1 population because the ionization cross section of the (ensemble of) states produced by IVR and VR are presumed to be lower than that of the SVL produced by direct laser excitation. Therefore, these effects result in the restoration (or partial restoration) of the fluorescence intensity which would be commensurate with the two photon absorption cross sections of the particular SVL from the ground state. Hence, in the absence of the up-pumping loss process (ionization) such as would be the case with infinitely fast IVR (or equivalently in the limit of infinite total pressure), the vibronic pattern in the TPF spectrum would converge to that of the OPA spectrum.

of the reprint

Figure 2 shows that, indeed, the application of a buffer gas results in the progressive restoration of the ABCO TPF spectrum to its MPI and OPA spectra. Alternatively, an attenuation in the effects of up-pumping on the TPF spectrum should be accomplished by a reduction in the laser flux; this

of the reprint effect, portrayed in Figure 3¹ convincingly supports the interpretation outlined above. These ideas are schematically portrayed in the following state diagram:



- where X is the ground state,
 A' is the vibronic level (SVL) in the first excited state (S_1), prepared by optical excitation,
 \bar{A} corresponds to the vibrationally redistributed levels in S_1 ,
 I is the ionic state (parent or fragment),
 σ_2 is the two photon absorption cross section for a transition from the ground state to a certain SVL of S_1 ,
 σ_I is the two photon ionization cross section from the SVL in S_1 to I,
 k_M is the rate constant for collision-induced IVR of the SVL of S_1 ,
 k_{IVR} is the intramolecular IVR rate constant of the SVL of S_1 ,
 M is the buffer gas pressure,
 k_f is the decay rate constant of S_1 , i.e., from A' or \bar{A} ,
 and F is the photon flux.

KINETIC ANALYSIS

The following section presents kinetic arguments in order to show that:

- (1) distortions in the TPF spectrum can arise from coherent ionization from S_1 ;
- (2) the MPI spectrum can, nevertheless, remain consistent with the OPA spectrum; and
- (3) the TPF spectrum is pressure and flux dependent, converging to the OPA spectrum in the limit of high total pressure or low flux.

Assuming that the excitation profile is a square pulse having a width T , and that the fluorescence lifetime ($1/k_f$) is $\gg T$ (where T is typically < 5 nsec), the populations of $A'(\nu)$, \bar{A} , and $I(\nu)$ are derived as:

$$\frac{dA'(\nu)}{dt} = \sigma_2(\nu) F^2 X - \sigma_1 F^2 A'(\nu) - (k_{IVR} + k_m M) A'(\nu)$$

$$\frac{d\bar{A}}{dt} = (k_{IVR} + k_m M) A'(\nu)$$

$$\frac{dI(\nu)}{dt} = \sigma_1 F^2 A'(\nu)$$

The fluorescence intensity, I_f , after time T is proportional to the total population of S_1 , namely, $A'(\nu)$ and \bar{A} , (ignoring possible ion recombination effects) and is given by:

$$I_f(t) \propto \frac{\sigma_2 F^2 X}{\sigma_2 F^2 + k_{IVR} + k_m M - \sigma_1 F^2} \left[\exp(-\sigma_2 F^2 T) - \exp(-(\sigma_1 F^2 + k_m M + k_{IVR}) T) \right. \\ \left. + \frac{k_{IVR} + k_m M}{\sigma_2 F^2} (1 - \exp(-\sigma_2 F^2 T)) - \frac{(k_{IVR} + k_m M)}{\sigma_1 F^2 + k_{IVR} + k_m M} (1 - \exp(-(\sigma_1 F^2 + k_{IVR} + k_m M) T)) \right] \quad (1)$$

This reduces to

$$I_f(T) \sim \left(\frac{\sigma_2 F^2 X^0}{\sigma_I F^2 + k_{IVR} + k_m M} \right) \left[1 + k_{IVR} T + k_m M T - \frac{(k_{IVR} + k_m M)}{\sigma_I F^2 + k_{IVR} + k_m M} \right] \quad (2)$$

Under the conditions that either $M \rightarrow \infty$ (very high total pressure), $k_{IVR} \gg \sigma_I F^2$ (very rapid intramolecular redistribution) or $\sigma_I F^2 \ll 1$ (negligible ionization), the fluorescence intensity expression becomes

$$I_f(T) \propto \sigma_2 F^2 T X^0 \quad (3)$$

and shows that the TPF spectrum goes as $\sigma_2(\nu)$, and should follow the OPA spectrum.

However, when $\sigma_I F^2 T > 1$ (saturation of the ionization step), and presuming also that $\sigma_I F^2 > k_{IVR}$ and $k_m M$, $I_f(T)$ becomes

$$I_f(T) \propto \frac{\sigma_2(\nu) X^0}{\sigma_I(\nu)} \quad (4)$$

where the laser frequency dependence of σ_2 and σ_I is explicitly indicated. Expression (4) shows that the TPF spectrum is distorted from the OPA spectrum (i.e., $\sigma_2(\nu)$) as a result of possible variations in $\sigma_I(\nu)$.

The number of ions N_I produced during excitation is given by

$$N_I = \sigma_I F^2 \int_0^T A'(t) dt \quad (5)$$

and reduces to the following (assuming that $\sigma_I \gg \sigma_2$)

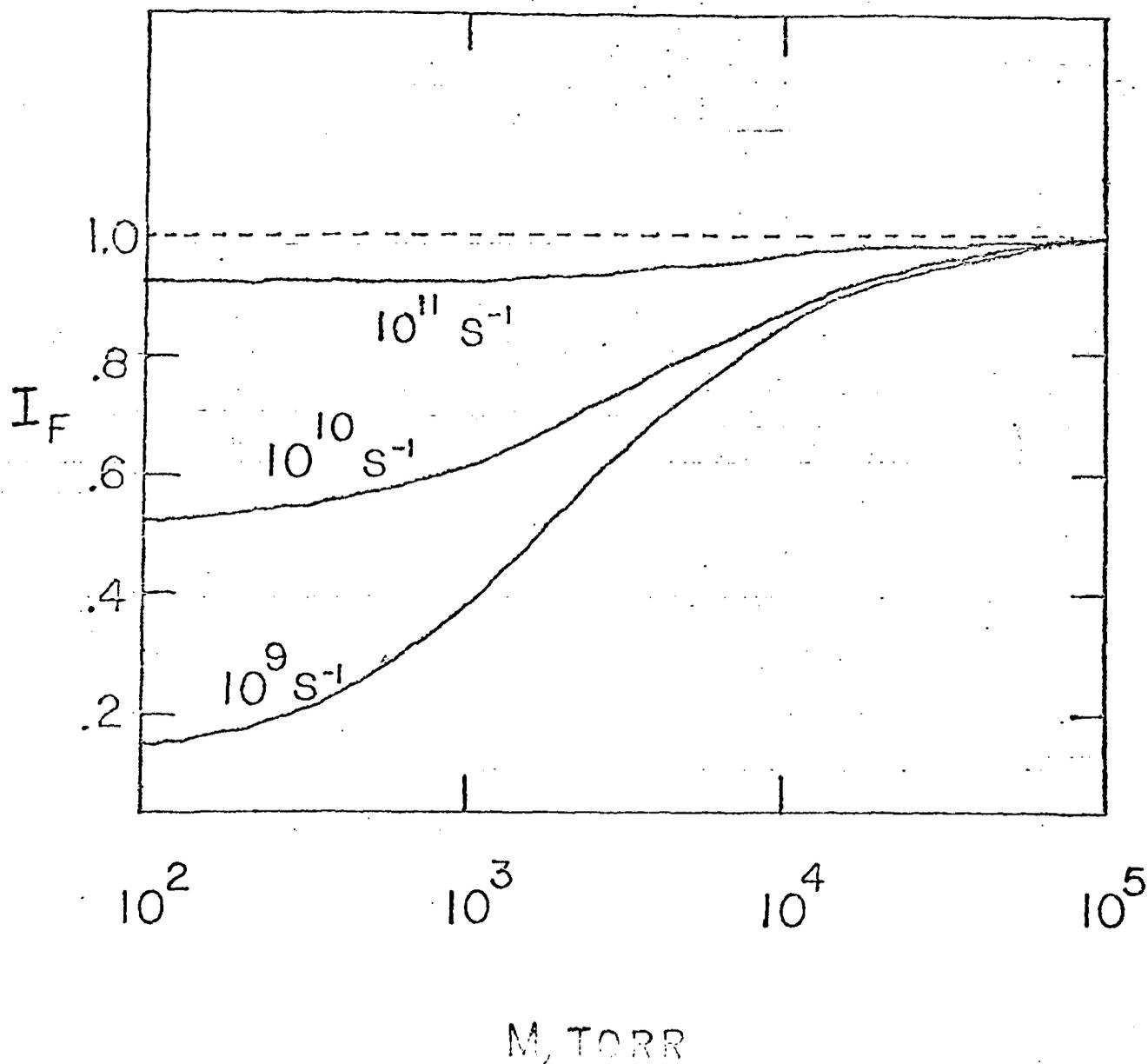
$$N_I \approx (\sigma_2 F^2 T - \frac{\sigma_2}{\sigma_I}) X^0 \approx \sigma_2 F^2 T X^0 \quad (6)$$

CONCLUSIONS

Equation (6) shows that the MPI spectrum can remain consistent with the OPA spectrum even though equation (4) holds, according to which the TPF and OPA spectra differ. This provides the rationale for the measurement of k_{IVR} values: namely, the determination of the pressure and flux dependence of the TPF spectrum and its comparison with the MPI spectrum. If this is performed for each of the vibrational modes (in progressions and sequences) seen in the TPF and MPI spectra, then the mode dependence of the rate of IVR can be achieved. In the least, the relative rates of this process can be discerned.

An example of the sensitivity with which k_{IVR} can be determined is indicated by a plot of equation (2) shown ^{on the next page,} where k_{IVR} ranges from $10^9 - 10^{11} \text{ sec}^{-1}$ and where reasonable values of other parameters have been used (e.g., $\sigma_{IF}^2 \sim 10^{10} \text{-sec}^{-1}$; $k_m \sim 5 \times 10^6 \text{ torr-sec}^{-1}$; $T \sim 5 \cdot 10^{-9} \text{ sec}$).

Another important and very useful application of this technique is that it can be used to infer structural information about the geometry of the parent ion of the molecular species being studied. This follows from the fact that the distortions in the TPF spectrum stem from the vibrational mode dependence of the ionization cross section of the \tilde{A} state. Accordingly, the distortions in the vibrational bands in the TPF spectrum are due to the fact that the vibrational modes whose nuclear displacements bring the \tilde{A} state of the molecule closer to the equilibrium configuration of the (ground state of) parent ion. This results in enhanced Franck-Condon factors for the ionization process from the \tilde{A} state. The excess vibrational energy produced in such a transition is then carried off by the ejected electron. Thus, an examination of the



Plot of equation (2), fluorescence intensity, I_f (arbitrary units), versus total pressure, M (torr) for various values of k_{IVR} .

TPFE spectrum in terms of those vibrational modes^ν which are active in inducing ionization from the \tilde{A} state reveals information about the equilibrium geometry of the ion. In a sense, this technique of differential TPFE/MPI spectroscopy forms a link with conventional photoelectron spectroscopy (PES) which, of course, deals with direct transitions between the ground states of the molecular and parent ionic species. Obtaining structural information about the parent ion directly from PES is often complicated by Franck-Condon restrictions in cases where the two states differ considerably in geometry. In using the \tilde{A} state as an intermediate in ionization, the technique lessens such problems.

Evidence of a state dependent depletion process in the two-photon fluorescence excitation spectra of saturated amines

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The two-photon fluorescence excitation (TPFE) spectra of regions of the \bar{A} states of two saturated amines 1-azabicyclo [2.2.2]octane (ABCO) and trimethylamine (TMA) are reported. These spectra are compared with the respective one-photon absorption (OPA), one-photon fluorescence excitation (OPFE), and multiphoton ionization (MPI) spectra for both molecules. For ABCO, this comparison clearly indicates major differences in both the vibronic band intensities and the amount of sequence structure present in the TPFE spectrum relative to the MPI, OPA, and OPFE spectra, which are all comparable. The "distortions" of the TPFE spectrum are interpreted in terms of a laser-induced \bar{A} state-dependent depletion process from \bar{A} which results in ionization. Pressure effects on the TPFE spectrum imply that the rate of this up-pumping process depends strongly upon the particular vibrational modes excited in the two-photon-induced $\bar{A} \leftarrow \bar{X}$ transition. A further implication of this interpretation is that the intramolecular vibrational relaxation time T_1 of some initially prepared levels is ≥ 100 ps. A kinetic model is presented which illustrates how (small) variations in the ionization cross sections of the \bar{A} state can have large effects on the TPFE spectrum but not on the MPI spectrum.

INTRODUCTION

The intense fields obtainable with focused laser radiation make possible several types of multiphoton spectroscopy.¹ These experimental techniques enable transition energies and strengths to be determined for electronic states which cannot be observed by conventional one-photon excitation. Multiphoton transition intensities have been valuable in studying spectroscopic and dynamical properties of polyatomic molecules. Kinetic models of competition between radiative and radiationless processes use these transition intensities to determine radiationless decay rates.²⁻⁴ In addition, different relative vibronic intensity patterns in excitations which are both one- and two-photon allowed have been used to investigate vibronic enhancement in electronic transitions.^{5,6} One technique which has been applied to the above problems is two-photon fluorescence excitation (TPFE) spectroscopy, which is useful in systems that luminesce efficiently. In this communication, we show that intensities in TPFE spectra can be interpreted in several new contexts and we discuss the implications in the saturated amines.

Active interest in both spectroscopic and photophysical properties of saturated amines has stimulated several recent multiphoton experiments. Colson and co-workers⁷ have made a more thorough and definitive assignment of the upper states of ammonia using multiphoton ionization (MPI) spectroscopy. An investigation of the MPI and TPFE spectra of the symmetric diamine, 1,4-diazabicyclo[2,2,2]octane (DABCO), by Parker and Avouris⁸ has led to the observation of the two-photon allowed, one-photon forbidden $\bar{A} \leftarrow \bar{X}$ transition.

The present study was motivated by the possibility of using two-photon selection rules to explore low energy states in flexible amines (i. e., those which undergo N-inversion) such as trimethylamine (TMA) and in cage amines such as 1-azabicyclo[2,2,2]octane (ABCO). It was anticipated that by applying both MPI and TPFE techniques to TMA and ABCO, further insight into the spectroscopic and photophysical properties of these molecules, and the amines in general, would be gained. For instance, the observation of a state lower in energy than the \bar{A} state in TMA could explain the anomalously vertical appearance and large Stokes' shift of the fluorescence spectrum which contrasts with the nonvertical nature of the absorption spectrum. While we have not found evidence of a low lying state in TMA, we have observed significant disparities in the TPFE spectra of both TMA and ABCO relative to their one-photon fluorescence excitation (OPFE) and MPI spectra. We attribute these differences to an ionization process which depletes some vibronic levels of \bar{A} preferentially, and becomes important with high photon fluxes. This explanation allows TPFE intensities to be used in deducing rates of intramolecular redistribution of vibrational energy and ionization cross sections of single vibronic levels. Applications to ABCO and TMA are discussed.

EXPERIMENTAL

Multiphoton excitation spectra were obtained using a nitrogen pumped dye laser with a pulse energy of 0.25 mJ and a duration of 5 ns, tunable between 360 and 700 nm. The laser beam was focused with a 4 in. focal length lens, except in the case of the low flux TPFE study of ABCO where a 14 in. lens was used with the sample cell, located ~ 5 in. in front of the focal point. The spectral linewidths in the multiphoton spectra of ABCO were laser-limited (~ 0.1 Å). The experimental apparatus used to obtain the MPI spectra has been described previ-

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ously.⁹ Briefly, the laser beam is focused between two parallel electrodes (biased at about 50 V) of a metal ionization cell containing the sample vapor. The resulting signal is amplified by a preamp and integrated by a Boxcar averager whose output is displayed on a strip chart recorder. The TPF emission is viewed at right angles to the excitation beam using a photomultiplier tube (Hamamatsu R106 U H), whose output is processed by the boxcar in the same manner as the MPI signal. The multiphoton fluorescence excitation spectra of TMA and ABCO were monitored at 287 and 270 nm, respectively, using bandpass filters (Corion bandpass ~ 37 cm^{-1}). That fluorescence from TMA was produced was confirmed by dispersing the emission, which matched the published fluorescence spectrum.¹⁰

The one-photon fluorescence excitation spectrum of ABCO was obtained using a D_2 filled nanosecond flash-lamp which was run at ~ 20 kHz and a modified time-correlated photon counting apparatus. The light was dispersed by a Jarrell-Ash 0.25 m monochromator having bandpass of 2.4 Å. Fluorescence was viewed through a 270 nm interference filter. A time to pulse height converter was used as a boxcar integrator with a time range of 400 ns. The acquisition time was ~ 3 h.

TMA (Matheson) and ABCO (Aldrich) were used without further purification. The spectra were obtained at 2 Torr ABCO pressure or 45 Torr TMA pressure, except where otherwise noted. For the ABCO vapor pressure used to obtain the multiphoton spectra, the system is collisionless on the time scale of the laser pulse but not on that of the fluorescence decay. No vibrationally unrelaxed emission was observed.

RESULTS AND DISCUSSION

Figure 1 contains the one-photon absorption (OPA),¹¹ one-photon fluorescence excitation (OPFE), MPI and TPF spectra of ABCO for the low energy part of the $\bar{A}-\bar{X}$ transition. The major bands in Fig. 1 are labeled A, B, C, ... for convenience, and Table I summarizes their energies and tentative assignments.¹² It can be seen from the higher resolution MPI spectrum that the same sequence structure accompanies each vibronic band. We assign the major sequence to the blue of each of the band origins as ν_{13} , the low-lying torsional mode, calculated to be 65 cm^{-1} in the ground state.¹³ This fre-

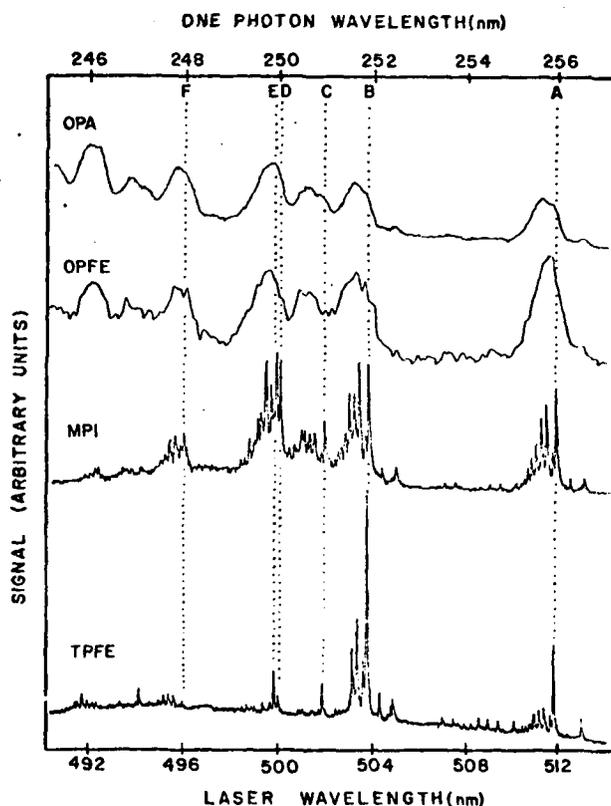


FIG. 1. A comparison of the one-photon absorption (OPA), one-photon fluorescence excitation (OPFE), multiphoton ionization (MPI), and two-photon fluorescence excitation (TPFE) spectra of ABCO vapor, 2 Torr, at 25°. A, B, C, D, E, and F indicate the positions of the band origins.

quency agrees well with that calculated from the observed intensity distribution in the MPI spectrum using the Boltzmann law. The sequence structure is not resolved in the low resolution OPFE or OPA spectra. However, the resolution is adequate for comparing the band intensities and widths of the four spectra. The band envelopes of the MPI spectrum match the respective features of the low resolution OPA and OPFE spectra, both with respect to their positions and relative intensities. The MPI spectrum of ABCO has been reported

TABLE I. Vibronic band assignments for the $\bar{A}-\bar{X}$ transition of ABCO.

Band	Laser wavelength, λ (nm)	$2/\lambda$, (cm^{-1})	Assignment ^a	$\Delta\nu$	ν'' ^b
A	511.88	39076	origin
B	503.85	39694	$12_0^1(\alpha_1)$	618	604(602)
C	501.98	39842	$11_0^1(\alpha_1)$	766	776(781).
D	500.12	39990	$\{33_0^1(\epsilon) \text{ or } 9_0^1(\alpha_1)\}^c$	914	965 or 990(969)
E	499.92	40006		930	
F	495.99	40323	12_0^2	1247	

^aVibrational mode notation taken from Ref. 13.

^bData obtained from IR spectrum (Ref. 12). Data in parentheses refer to hot bands seen in the MPI spectrum, this study.

^cA definitive assignment of these bands is not warranted at the present.

by Parker and Avouris,¹⁴ who also find that the MPI spectrum correlates well with the OPA spectrum. The TPFE spectrum of ABCO, however, reveals striking differences relative to the other three spectra. Strong suppression of the major sequence relative to the corresponding band origin is observed in all of the TPFE bands. Higher members of the major sequence are attenuated more strongly, producing narrower bands in TPFE relative to MPI, OPFE, and OPA. Furthermore, the relative vibronic band intensities are markedly different, with A, C, and especially D and E being much weaker relative to B in TPFE. Disparities in TPFE spectra have been noted in the literature before, both with respect to OPA spectra and to MPI spectra. The mechanisms which have been invoked to explain these differences are vibronic induction and radiationless relaxation, respectively.

Vasudev and Brand have discussed vibronic enhancement in TPFE spectra^{5,6} in connection with the TPFE spectrum of fluorobenzene, in a state in which both one- and two-photon absorption are allowed. As they point out, a zero order approximation of nonresonant two-photon absorption strengths allows the vibrational overlap integral between initial and final vibrational states to be separated from electronic contributions to the transition moment. One therefore expects relative vibronic absorption intensities to be the same in one- and two-photon excitations so that TPFE and OPFE spectra should match. Vibronic enhancement resulting from the breakdown of the Born-Oppenheimer approximation is possible and might be different for one- and two-photon absorption but this effect should be unimportant with α_1 vibrations as in ABCO. Because the MPI spectrum closely agrees with the OPA and OPFE spectra (*vide supra*), it is unlikely that the discrepancies in the TPFE spectrum of ABCO arise from vibronic effects on the absorption intensities in the two-photon process.

State selective radiationless decay was shown to explain the difference between the TPFE and MPI spectra of the \tilde{C} state of NO,⁴ where rotational predissociation competes effectively with luminescence but not ionization. However, radiationless processes cannot account for the "distortions" of the TPFE spectrum in ABCO. The fluorescence quantum efficiency of ABCO is fairly large,¹⁵ although excimer formation is known to occur at sufficiently high ABCO pressures. Also, the OPFE spectrum follows the OPA spectrum very closely, suggesting that any photophysical or photochemical losses are only weakly energy dependent. This conclusion is corroborated by the TPFE spectrum of the same region of ABCO when excimer fluorescence is monitored, since it closely mirrors the TPFE spectrum of the monomer. The intensity differences between the TPFE and MPI spectra of the monomer are very highly structured in energy, and this would be uncharacteristic for radiationless processes. It would be difficult on this basis to rationalize why *all* of the sequence bands are attenuated in TPFE and why some lower energy levels of \tilde{A} diminish in intensity relative to higher energy levels of \tilde{A} in the TPFE spectrum.

The explanation we propose for distortions in the

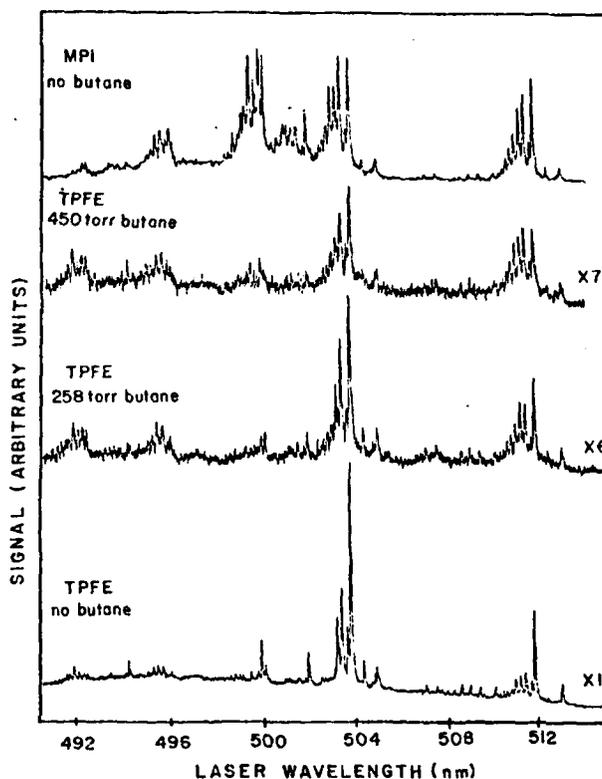


FIG. 2. Pressure effects on the TPFE spectrum of ABCO. The lowest spectrum is the TPFE spectrum taken with no added butane. The two above it are the TPFE spectra obtained with 258 and 450 Torr of added butane. The relative intensities of the TPFE spectra are indicated to the right of each spectrum. The MPI spectrum is presented for comparison.

TPFE spectrum of ABCO involves laser-induced depletion of the \tilde{A} state population. To test this hypothesis, TPFE spectra of ABCO were taken with added buffer gas (*n*-butane). Since the transition origin is attenuated in TPFE relative to MPI less than many of the other bands, collisional relaxation which is fast enough to compete with up-pumping should restore some intensity to bands attenuated more than the origin. TPFE spectra at 0, 258, and 450 Torr of added *n*-butane are reported in Fig. 2 and demonstrate that the sequence intensities are indeed restored. Even at 500 Torr, however, up-pumping only appears to compete efficiently with collisional relaxation in some bands so that up-pumping rates of 10^{10} s⁻¹ and higher are in effect, where we assume unit efficiency ("strong") collisions with a cross section corresponding to 50 ns Torr. As expected, a similar restoration of relative intensities to TPFE bands occurs when the laser flux is lowered. The intensity dependence of the fluorescence is close to linear and goes up with decreased laser intensity, as expected (see experimental section) when field-induced loss processes are occurring. At sufficiently low flux, the intensity dependence becomes quadratic, and the spectrum is almost identical to the MPI spectrum (Fig. 3).

TPFE measures the fluorescence from the \tilde{A} state, while MPI detects the ions produced by further up-pump-

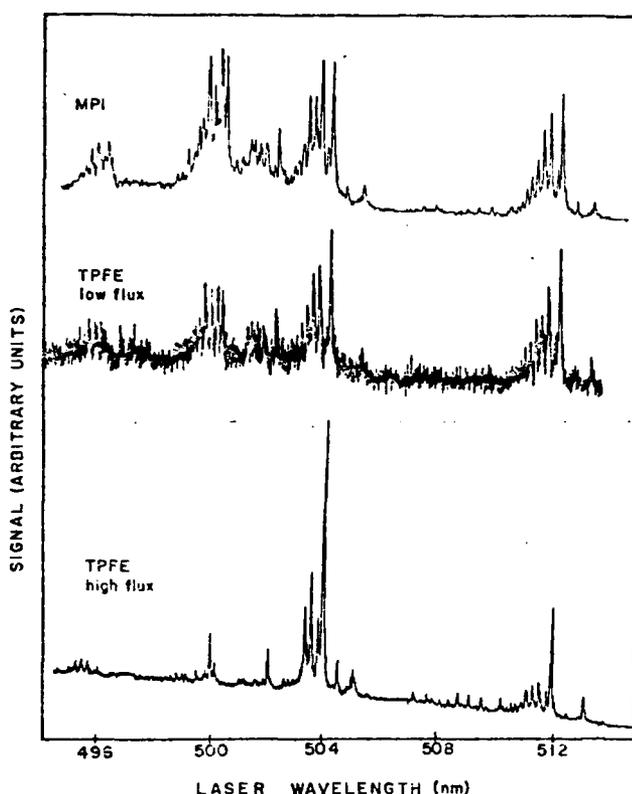


FIG. 3. Intensity dependence of the TPF spectrum of ABCO. The lowest and middle spectra are taken at high and low flux conditions, respectively (see Experimental section for details). The MPI spectrum is presented for comparison.

ing from the \bar{A} state. A simple kinetic model illustrates how it is possible for TPF and MPI spectra to be affected differently by laser-induced depletion of \bar{A} . Ackerhalt and Eberly¹⁵ have shown that such a model will be valid in a multistep absorption where each step has successively increasing transition rates and the final step is irreversible, as in ABCO ionization. Assuming no depletion of \bar{X} , the appropriate rate equations for a two-photon absorption and subsequent two-photon ionization in ABCO are

$$\frac{dA(t)}{dt} = \sigma_2 F^2 X - \sigma_1 F^2 A(t) \quad (1)$$

and

$$\frac{dI}{dt} = \sigma_1 F^2 A(t) \quad (2)$$

where X is the population of \bar{X} ; A is the population of level in \bar{A} ; σ_2 is the two-photon absorption cross section for $\bar{A} - \bar{X}$ (cm^4/s); σ_1 is the two-photon ionization cross section for level in \bar{A} ; F is photon flux ($\text{photons}/\text{cm}^2/\text{s}$); and I is the number of ions produced. As long as the fluorescence lifetime is much longer than the pulse time T , the population of \bar{A} after T should be proportional to fluorescence and is given by

$$A(T) = (\sigma_2/\sigma_1) [1 - \exp(-\sigma_1 F^2 T)] X \quad (3)$$

For small $\sigma_1 F^2 T (< 1)$, this reduces to the expected value of $A (\approx \sigma_2 F^2 T X)$ and is unaffected by ionization. However, for $\sigma_1 F^2 T \geq 1$, saturation of the ionization step leads to values of $A \approx (\sigma_2/\sigma_1) X$ which are inversely proportional to the ionization rate. When the ionization step is saturated, the expression for number of ions

$$I = \sigma_2 F^2 X \left\{ T - \frac{1}{\sigma_1 F^2} [1 - \exp(-\sigma_1 F^2 T)] \right\} \quad (4)$$

reduces to

$$I \approx \left(\sigma_2 F^2 T - \frac{\sigma_2}{\sigma_1} \right) X \approx \sigma_2 F^2 T X \quad (5)$$

and measures precisely the population originally excited to \bar{A} but is insensitive to σ_1 .

For $\sigma_1 F^2 T \geq 1$, then, we can expect the MPI spectrum to be "true" to the original absorption strengths, but the TPF spectrum would be distorted due to the energy (or state) dependence of σ_1 . We can infer from our pressure studies that the up-pumping rates (i.e., $\sigma_1 F^2$) from some of the bands are close to or higher than 10^{10} s^{-1} . This means that we are well into the regime of saturated ionization for 5 ns pulse times. For a typical photon flux of $10^{23} \text{ photon}/\text{cm}^2/\text{s}$, ionization cross sections would be on the order of $10^{-48} \text{ cm}^4/\text{s}$ or larger, quite large for two-photon transitions.

As noted above, the major sequence associated with each of the vibronic bands in the TPF spectrum is attenuated relative to its origin. This observation suggests that the process which modulates the ionization cross sections and hence produces distortions in the TPF spectrum is a geometry or vibronic mode dependence to σ_1 rather than simply variations in σ_1 due to the laser wavelength or excess vibrational energy in the \bar{A} state. To this point, we have implicitly assumed that the depletion process is coherent two-photon ionization rather than one-photon absorption. Since one-photon absorption to a higher bound Rydberg state would be vertical, we would expect variations in the depletion rate with laser wavelength because different vibrational modes (i.e., geometries) of the upper state are accessed. Any spectral structure due to variation of upper state character would appear as a wavelength modulation of the distortions in the TPF spectrum. Since depletion rates vary with vibrational mode character in \bar{A} and not independently with laser wavelength, we infer that the upper state nuclear geometry does not change appreciably with laser wavelength. In ionization, however, the absorption can be spectrally diffuse even when the final geometry is fixed because the excess energy can be released with the ejected electron. Therefore, we presume that the predominant product is ground state ABCO ion. This interpretation means that our spectrum contains the kind of information one would get from a relaxed emission spectrum of the ion to \bar{A} , if such a spectrum were possible. Those vibrational modes which bring the potential surfaces of the \bar{A} state of ABCO closer to the equilibrium configuration of the \bar{X} state of the cation are active in the up-pumping process. Accordingly, the assignment of the vibrations preferred in \bar{A} state ionization should give structural information about the ion.

Moreover, a more detailed pressure study of the TPF E spectrum should enable one to determine the relative up-pumping rates of these "labile" modes. This process can be thought of as vibronic photosclective photoionization. This information thus complements the conventional photoelectron spectrum (PES) which measures ionization cross sections from the \bar{X} state of the molecule.

There are advantages to this technique in ABCO where the PES is highly congested,^{16,17} probably due to numerous sequence excitations. The effect on the ionization cross section of bringing the potential surfaces of the ground states of the parent and of the ion closer together (as in excitation to \bar{A}) can be illustrated by comparing the PES of ABCO with that of 1-azabicyclo[3, 3, 3]undecane (ABCU). The C-N-C bond angles of ABCO and ABCU are about 109° and 115°, respectively, whereas the relaxed ion has a bond angle of 120°. The PES of ABCU is much more vertical than that of ABCO, and the differences between vertical and adiabatic ionization potentials for these amines have been reported by Aue *et al.* to be 0.07 eV for ABCU and 0.55 eV for ABCO.¹⁸

The decreased intensities of the major sequences observed in the TPF E spectrum *vis-à-vis* the MPI spectrum suggest that the mode which is excited in these transitions is strongly coupled in subsequent transitions to the ion from the \bar{A} state. We assign this sequence transition to excitations of the torsional mode, in analogy with the assignment made for DABCO.⁸ Similar geometrical arguments should apply to the band systems A, B, C, Judging from the intensities of the band origins, vibronic band B, which is associated with ν_{12} , the mode involving the flattening of the N atom-bearing part of the cage, shows no more propensity to ionize than the electronic origin, band \bar{A} . This suggests that the degree of planarity achieved in the \bar{A} state may be similar to that in the ion.

Bands C, D, and E are all very strongly suppressed in the TPF E spectrum and are relatively resistant to pressure effects. This implies that these states have much larger ionization cross sections. These bands are associated with excitations of the skeletal modes ν_{11} , ν_{33} , and ν_3 (see Table I). A normal coordinate analysis of ABCO suggests that these modes carry out cage distortions such as the flattening of the C-H portion of the cage, and the extension of the C-C bridgehead bonds.

There is an extremely important implicit assumption made in attributing variations in ionization rate to geometric characteristics of the vibronic levels of \bar{A} . Specifically, the excess vibrational energy in \bar{A} must remain in the mode of interest for a time long compared to the reciprocal of the ionization rate. The coupling time to the intramolecular heat bath T_1 must be much greater than $1/\sigma_1 F^2$, in our case something more than 100 ps for some of the vibrational levels. Careful pressure and laser intensity studies can, in principle, set bounds for T_1 for single vibronic levels of excited states in this manner. Currently, this information is fairly difficult to obtain.¹⁹

We now turn to a discussion of the results obtained for TMA. The lack of vibronic detail in the absorption

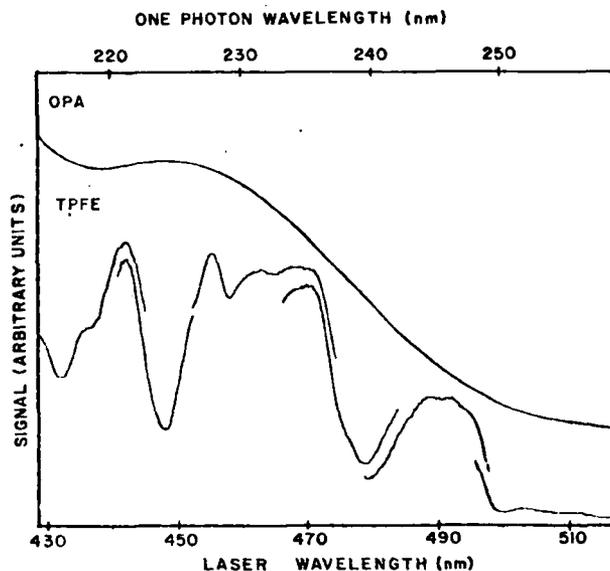


FIG. 4. The OPA and TPF E spectra of trimethylamine vapor. Each of the segments of the TPF E spectrum is obtained with the use of a different laser dye. All dyes were used in their respective maximum intensity, or flat regions. The TPF E spectrum is not corrected for changes in dye intensities.

spectrum of TMA (as well as in the other flexible amines) precludes a definitive characterization of the $\bar{A} - \bar{X}$ transition. Nevertheless, Matsumi and Obi²⁰ recently reported the presence of very subtle vibrational structure in the low energy portion of the $\bar{A} - \bar{X}$ transition. We examined the MPI spectrum of TMA and found no evidence of structure, although this technique might make direct observation of weak vibrational structure difficult to extract. There is no evidence for a lower lying state than \bar{A} in the TPF E or MPI spectra. The TPF E spectrum of TMA (see Fig. 4) does, however, possess structural features not seen in either the MPI or OPA spectrum.

Although the TPF E spectrum shown in Fig. 4 must be regarded as qualitative because the spectral features are diffuse compared to the relatively narrow lasing range for dyes in this region, it is clear that disparities between the TPF E and OPA spectra exist. These disparities are invariant with addition of buffer gas (760 Torr *n*-butane) or TMA self-pressure (up to 600 Torr).

The interpretation of the TMA TPF E spectrum is probably the same as that suggested above for ABCO. Accordingly, the "structure" in the TPF E spectrum is caused by laser-induced state dependent depletion of the \bar{A} state which distorts the vibronic envelope of the OPA spectrum. This is consistent with Zapka and Schäfer's²¹ work which demonstrates that \bar{A} state ionization in TMA is a very efficient process. Kasatani *et al.*²² have recently reported the TPF E spectrum of TMA and it shows no distortion in this region, probably because it is obtained with microsecond laser pulses of comparatively low flux. As we have shown above, under low flux conditions, the TPF E spectrum of ABCO also closely resembles its OPA spectrum. The intensity dependence

of our TMA TPFE spectra is close to linear, as opposed to the squared dependence observed by Kasatani *et al.* in their study. Again, as we explained above for ABCO, this is expected when laser-induced loss processes compete with relaxation and subsequent fluorescence.

CONCLUSIONS

We have found that in ABCO, the systematic intensity differences between the TPFE and other spectra of the $\bar{A} - \bar{X}$ transition are caused by laser-induced depletion of the \bar{A} state at rates greater than 10^{10} s^{-1} , corresponding to two-photon ionization cross sections from A of greater than $10^{-46} \text{ cm}^2 \text{ s}$.

In addition, regularities in the relative strengths of the TPFE intensities suggest a correlation between geometry and ionization cross section and show that energy remains in the initially excited modes for longer than 100 ps. Vibrational assignments used with intensity differences indicate a twisted ionic configuration for ABCO. The same qualitative behavior is evident in TMA and illustrates that studies of intensities in multiphoton spectra can be of general use for deducing not only spectroscopic but also dynamical and structural information.

With the high fluxes which characterize the lasers needed to perform multiphoton spectroscopy, it is not in general possible to interpret fluorescence excitation and absorption spectra as in conventional one photon spectroscopy. To attribute differences between TPFE spectra and spectra reflecting two-photon absorption to radiationless processes requires independent information. Laser-induced depletion of excited population can be important in modulating intensities in TPFE, and pressure and power dependence studies can clarify the extent to which this is the case. Ionization cross sections can be heavily dependent on the vibrational level excited and, in the regime where the ionization is close to saturation, this results in distortions of the TPFE spectrum relative to the OPFE spectrum. To the extent that variation of ionization cross section with vibrational level reflects a geometric propensity to ionize, one can learn about the geometry of the ion and can set a lower limit

on the time T_1 during which energy is localized in that vibration.

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